THE ANALYTICAL CHEMISTRY OF INDUSTRIAL POISONS, HAZARDS, AND SOLVENTS

SECOND EDITION

by M. B. JACOBS

CFTRI-MYSORE
1703
Analytical chemi

1703 ① gas volume
② absorbers ③ absorbents
④ dust ⑤ silica ⑥ toxic
metals ⑦ poisonous compounds
⑧ carbon monoxide
⑨ cyanides ⑩ nitriles
⑪ solvent vapors ⑫ hydrocarbons
⑬ alcohols ⑭ ethers
⑮ esters ⑯ Ketones [illegible]
⑲ paraffins substances
⑳ toxic compounds
㉑ "

CHEMICAL ANALYSIS

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Volume I

The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents

Second Edition, Revised and Enlarged

by MORRIS B. JACOBS

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Second Edition
Revised and Enlarged

1949

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PREFACE
to the Second Edition

In the eight years that have passed since the publication of the first edition of this book there has been great progress in the field of industrial hygiene. It has been my objective to incorporate in the new edition of this book this progress insofar as it applies to analytical chemistry. This has entailed substantial changes in every chapter in the light of new knowledge. An attempt has been made to cover the field of analytical chemistry of industrial poisons exhaustively. Certain material has been deliberately included to supply historical background and thus increase its usefulness where the text is being used for educational purposes.

Brooklyn, New York, 1949 MORRIS B. JACOBS

From the Preface to the First Edition

Although the literature of industrial hygiene is large, there are few books dealing with the chemical aspects of the subject. The increase in industrial hygiene work particularly in the analytical chemistry of industrial poisons, hazards, and solvents has been marked since World War I. That this is especially true of the United States of America is evidenced by the numerous citations throughout the text. The publications of the United States Public Health Service, the United States Bureau of Mines, the United States Department of Labor and the Industrial Hygiene Division of the New York State Department of Labor were of inestimable value in the preparation of this book. The American Journal of Public Health, the Yearbook of the American Public Health Association, the Journal of Industrial Hygiene and Toxicology, Industrial Medicine, Industrial and Engineering Chemistry Analytical Edition, and the British Analyst were also valuable sources.

It is the hope of the author that this book will be a contribution to analytical chemistry in industrial hygiene. It should be useful in industry, insurance, education, governmental regulation, research, hospitals, and for chemists, toxicologists, and physicians.

The author wishes to thank particularly Dr. S. Moskowitz for his valuable suggestions and for reviewing the manuscript. The advice of Dr. Ernst P. Pick on the aspects concerning the physiological response of industrial substances is gratefully acknowledged. Thanks are extended to Professors C. V. King and H. Taub for reviewing portions of the manuscript. The valuable assistance of Margaret Jacobs and Roberta Leah Jacobs in reading proof and of Berenice Anita Jacobs in the preparation of the index is acknowledged.

The author has tried to give adequate acknowledgment for the use of illustrations, methods, procedures, tables, etc., either in the text or at the end of the chapter. If any reference is omitted, such omission is entirely unintentional. The author will be only too happy to correct such omissions if brought to his attention.

Brooklyn, New York, 1941 MORRIS B. JACOBS

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Definitions of Terms and Explanatory Notes

1. The term water used in the methods means distilled water.

2. The terms alcohol and ether refer respectively to 95 per cent ethyl alcohol and to ethyl ether.

3. The following reagents, unless otherwise specified or qualified in the text, have the approximate strength stated and conform in purity with the requirements of the United States Pharmacopoeia.

sulfuric acid	specific gravity 1.84
hydrochloric acid	specific gravity 1.184
nitric acid	specific gravity 1.42
fuming nitric acid	specific gravity 1.50
glacial acetic acid	specific gravity 1.048 (25°C.)
hydrobromic acid	specific gravity 1.38
phosphoric acid	85 per cent strength by weight
ammonium hydroxide	specific gravity 0.90

4. All other reagents and test solutions, unless otherwise described in the text, conform to the specifications of the United States Pharmacopoeia or of the American Chemical Society. When the anhydrous salt is intended to be used, it is so stated; otherwise the salt referred to is the crystallized product.

5. In the expressions (1:2), (5:4), etc., used in connection with the name of a reagent, the first numeral indicates the volume of the reagent used, and the second numeral indicates the volume of water. For example, hydrochloric acid (1:2) means a reagent prepared by mixing one volume of hydrochloric acid with two volumes of water. When one of the reagents is a solid the expression means parts by weight, the first numeral representing the weight of the solid reagent and the second numeral the weight of water in similar units.

6. In making up solutions of definite percentage, it is understood that x grams of substance is dissolved in water or other solvent and made up to 100 ml. Although not theoretically correct, this procedure will not result in any appreciable error in any of the methods given in this book.

7. All calculations are based on the table of international atomic weights.

8. The following abbreviations are used and have the indicated meaning:

ml.	milliliter	c.f.m.	cubic feet per minute
l.	liter	l.p.m.	liters per minute
C.	Centigrade degrees	μ	micron
F.	Fahrenheit degrees	S.T.P.	standard temperature and pressure
N	normal, with reference to solutions	e.m.f.	electromotive force
mm.	millimeters	r.p.m.	revolutions per minute
mg.	milligrams	lb.	pound
mg./l.	milligrams per liter	sp.gr.	specific gravity
ppm.	parts per million	r.e.m.	roentgen equivalent man
mm^3	cubic millimeters		

The abbreviations of periodicals, bulletins, circulars, leaflets, etc., referred to in the footnotes follow, in general, the system of *Chemical Abstracts*.

9. In the use of the expression "parts per million of x," it is understood that the expression means parts of x per million parts of air. The author has tried to differentiate when this expression is used with reference to a solution, by the statement "parts of x per million of solution."

10. As a general rule, the author has given the preparation of the reagent immediately following the naming of the reagent in the body of the method rather than giving a numbered or lettered list, before giving the method. The author has found that in reading methods it is a nuisance to read, "and then add 5 ml. of reagent A . . ." Very often the analyst must look back to the beginning of the section or paragraph to find out what reagent A is. Only in the case of very complex reagents is the method of preparation detailed in advance.

The proper way to proceed is to read the method at least twice to completion. On the third reading the reagents are prepared. Then if the determination has never been performed by the analyst before, known control and blank samples are used. Only after some experience with known samples has been obtained should the test samples be analyzed.

CHAPTER I

Industrial Hygiene and Industrial Poisons

1. Introduction

The vastly expanded use of chemicals both in industry and in the home within the past five decades has made the study of these chemicals and their effect on our health of immediate importance. One need only think of the greatly increased use of organic solvents, refrigerants, fumigants, rodenticides, insecticides, fungicides, germicides, diluents and plasticizers, plating solutions, and the possible employment of fissionable material to realize how widespread the use of chemicals is and how closely they affect us both in commerce and at home.

The World War of 1914–1918 very likely was the greatest single factor in the introduction of care in the manufacture of organic materials, for it drew an impressive picture of the dangers of gases and vapors. The war certainly stressed the need for protection against these hazards. The huge increase in the production of organic chemicals to meet the needs of war for explosives, chemical agents, and other war matériel made it necessary to learn how to protect both workers and soldiers using or subjected to this matériel. The precautionary measures, developed as a result of World War I, received even greater emphasis in World War II, particularly in measures which had to be devised to protect workers engaged in the manufacture of fissionable material and other war matériel such as poison gas and bacterial toxins.

It has become increasingly evident that the control, regulation, and prevention of industrial hazards lie in the hands of the physician, sanitary engineer, or inspector, and the chemist or chemical engineer. Governmental agencies must necessarily play their part. The earliest and unquestionably the most important progress of the past in recognizing, treating, and remedying industrial hazards was made by the medical profession. In more recent years the role of the sanitary engineer and the chemist has become relatively more important. Though the control and regulation of industrial hygiene should, perhaps, remain in the hands of the physician, the prevention of industrial hazards is mainly a function of the engineer, the chemist, and, in more recent years, even the physicist.

The chemist supplies the necessary, analytical devices and methods. His results indicate how much of a toxic, noxious, or hazardous material is present. The ability to estimate quantitatively the amount of a toxic or otherwise hazardous material is a most important factor in the lessening of any menace to the health of employees. Based upon these quantitative analytical results, the corrections and improvements needed to alleviate a hazardous condition can be made. The knowledge of the amount and location of contamination is of inestimable value in designing the means of prevention and elimination of the poison. In testing the air of a large garage, it was found that 10 feet away from the exhaust of a running car, there were 1,000 parts of carbon monoxide per million parts of air present (0.1 percent by volume), whereas 30 feet away from the same car it was impossible to get a positive test for this poisonous gas.[1] The prevention of hazard in such an instance and in analogous cases needs special design and treatment that can more readily be obtained with the aid of the analysis made by the chemist.

Where new materials or substances are developed or where well-known substances are used for new procedures, the chemist can devise methods for the estimation of these substances, taking into consideration the methods of use. A veritable host of new materials is being developed.

2. Industrial Hygiene

Industrial hygiene is an applied science, as distinguished from the theoretical sciences such as mathematics or physics. It is defined[2] as the art and science of the preservation and improvement of the health and comfort of workers. It therefore involves primarily a program of health conservation and accident and occupational-disease prevention. Such a program necessarily extends beyond prevention of accidents and occupational diseases; it includes also the broad subject of the health of the worker. It is obvious that some of the problems arise from the nature of the industrial environment itself—namely, the control of poisons, dusts, excessive temperatures and humidities, defective lighting, noise, overcrowding, and general plant sanitation. The problems also involve such factors as hours of work, fatigue, communicable diseases in the factory, mental health, and personal hygiene. An industrial-hygiene program thus necessitates the cooperation of a number of professional personnel including the physician, engineer, chemist, statistician, nurse, and dentist.

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[1] R. R. Sayers and S. Davenport, *U. S. Pub. Health Service, Bull. 195* (1937).

[2] *Ind. Hyg. Newsletter, 1,* No. 4, 13 (1947).

Its aim is to protect and improve the health of workers. As an applied science, it has a number of major subdivisions, among which may be mentioned:

Industrial Medicine, which includes industrial medical care, prevention of industrial illness, hospitalization, and medical aspects of compensation.

Industrial Mental Hygiene, which includes behavior of workers and the mental state and health of workers.

Industrial Management, which includes hours of labor, rest periods, adequate food, supervision and the general economic relationships of laborers and their health.

Industrial Sanitation, which includes environment of the worker, buildings, machinery, air conditions, ventilation, exhaust, and, in general, all engineering aspects.

Industrial Hazards, which includes detection and estimation of hazards; prevention, diminution, and elimination of hazards, toxicants, etc.

Our main study will be with the one section of industrial hazards that deals with the detection, estimation, and determination of industrial poisons and other harmful industrial substances.

Historical Background

Poisons have been known and used from time immemorial. The Bible and ancient myths make reference to them. But poisoning due to occupation was not so clearly defined in the minds of ancient and medieval men. Hippocrates (about 460–357 B. C.) described lead poisoning as an occupational disease only in the smelting of metals. Vitruvius Pollio (70–16 B. C.), a Roman architect, engineer, and author, observed that lead poisoning resulted from drinking water that had been collected from lead-covered roofs, transferred to lead storage cisterns, and then fed to the public through lead pipes. The poisonous qualities of sulfide ores and carbon monoxide were known to the Greeks and Romans. Avicenna (980–1036), the Arabian writer of the eleventh century, recognized the poisonous properties of arsenic trioxide. In somewhat later medieval times, it was known that arsenic and lead compounds were toxic. The first printed book on industrial hazards, *Morbi metallici,* was written by Ulrich Ellenbog, of Feldkirch, about 1524 and discussed the hazards of lead and mercury. In the seventeenth century, Ramazzini (1633–1711 born in Carpi, died in Padua), regarded as the "father of industrial hygiene," wrote *De Morbis Artificum*[3] (Diseases of Tradesmen).

Though some few books were written and some physicians were aware of the problem, actually there was practically little known, done, or thought with respect to industrial hygiene until recent times.[4] Dr. Charles Turner Thachrah, a British physician, was one of the earliest observers and commentators on industrial hazards and hygiene. He wrote a short but significant book, published in 1831, entitled *The Effects of the Principal Arts, Trades, and Professions, and of Civic States and Habits of Living on Health and Longevity, with a Particular Reference to the Trades and Manufactures of Leeds, and Suggestions for the Removal of Many of the Agents Which Produce Disease and Shorten the Duration of Life.*[5]

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[3] H. Goodman, *Diseases of Tradesmen by Bernadino Ramazzini,* Medical Lay Press, New York, 1933.

Had England listened to this pioneer for the betterment of working conditions, the cause of safe and adequate industrial care would have been advanced at least fifty years. It was not until much later that interest in this major problem was again aroused. Dr. Thackrah unfortunately died young and many of his ideas died with him.

A direct result of the expansion attributable to the industrial revolution in England was the appalling sanitary conditions described in a report to Parliament in 1842. Edwin Chadwick[6] pioneered in eliminating these evils.

In the United States, as early as 1837, McCready[7] stressed the influence of industrial activity on disease. The first state in the United States to pass any industrial hygiene legislation was Massachusetts, in 1852.

Hermann Eulenberg wrote a text on the noxious and piosonous gases in 1865 (*Lehre von den Schaedlichen und giftigen Gasen,* Braunschweig bei Vieweg) and later followed this with a more general text on industrial hygiene (*Handbuch der Gewerbe—Hygiene auf experimentelles Grundlage,* Verlag von August Hirschwald, 1876).

The United States in the past lagged behind other nations in its interest in industrial hygiene but interest was aroused in the second decade of the twentieth century and now matches that of any other country. Governmental regulation of industrial hazards in the United States is nevertheless relatively a recent development. One need but recall that it was only in 1912 that the Esch law was passed. This law prevented the use of white phosphorus (yellow phosphorus) in matches by placing a prohibitive tax on its use for this purpose. This substance is the cause of the horrible phossy jaw of match workers.

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[4] T. M. Legge, *J. Ind. Hyg., 1,* 475 (1919–20).

[5] T. M. Legge, *J. Ind. Hyg., 1,* 578 (1919–20).

[6] R. T. Legge, *Am. Ind. Hyg. Assoc. Quarterly, 7,* 5 (1946).

[7] B. W. McCready, *On the Influence of Trades, Professions, and Occupations in the United States in the Production of Disease (1837),* Johns Hopkins, Baltimore, 1943.

It has been known for centuries that workers in dusty atmospheres were less healthy than those not exposed to dust. More particularly, it was known that atmospheric dust was a cause of pulmonary fibrosis by investigators interested in industrial hygiene and occupational diseases. The United States Public Health Service and the Bureau of Mines, however, did not interest themselves in this problem until 1914. These agencies published the first report of their joint study made among the hard-rock miners of the Joplin (Missouri) district in 1915.[8] Since that report much important work has been done by these agencies in the study of this hazard and in developing devices and procedures for its elimination. The term "silicosis," which is applied to the illness brought about by exposure, generally over a period of years, to inhalation of silica dust, is now a household word. To some medical authorities, this term is preferable to the term "miners' phthisis," because it indicates the chief cause of the disease and does not stress the wasting symptoms, which may not always be present in a silicosis victim. The condition of pulmonary silicosis, one of many types of pneumonokonioses, develops more rapidly the more intensive the exposure and the finer the particles of silica dust encountered.

It is probable that organic dusts do not cause pneumonokonioses, but unquestionably silicosis is not limited to mines, quarries, and knife factories. In almost every modern factory in which steel and iron are principal raw materials for the manufacture of other materials, there is the possibility that some steps in the process of manufacture will present an industrial hazard because of the silica dust produced.[9]

An analogous type of pulmonary occupational disease is known as "asbestosis." It is caused by long exposure to asbestos dust.[10]

3. *Governmental Problem*

That industrial hygiene and the prevention of industrial hazards in the United States became a recognized major problem is clear from the following quotation from an address given by Dr. R. R. Sayers, Chief,

[8] L. Greenburg and J. J. Bloomfield, *U. S. Pub. Health Service, Reprint 1528* (1935).
[9] J. A. Britton, *J. Ind. Hyg., 6,* 199 (1924).
[10] R. R. Sayers and W. C. Dreessen, *Am. J. Pub. Health, 29,* 205 (1935).

U. S. Bureau of Mines, on "Industrial Hygiene Activities in the United States."[11]

> "The United States Census for 1930 shows that, at that time, there were approximately 49 million persons gainfully employed in the United States. Of this number, manufacturing, mechanical and mineral industries accounted for nearly 15 million workers. If the term "Industrial Hygiene" means the protection of the health of the worker, it is at once apparent that it is a major problem in public health.
>
> "More important than specific occupational diseases associated with the industrial environment is the fact that the incidence of other diseases as tuberculosis, pneumonia and degenerative conditions are greater among the industrial workers than the general population. It has also been shown that the life expectancy of the industrial worker is less than that of the non-industrial worker.
>
> "In recent years large industrial establishments have contributed much toward the protection of the health of their workers. However, as nearly 90 per cent of the plants in the United States employ less than 100 persons, many establishments are not prepared to handle effectively the problem of industrial hygiene alone. It would seem, therefore, that the protection of the health of our workers is indeed an important health function and one which can be handled best through a governmental agency, such as a State or local department of health cooperating with the employers and workers.
>
> "Responsibility for safeguarding the health of industrial workers rests chiefly with State and local governments. The Federal Government's agencies concerned with industrial hygiene are engaged in collection and dissemination of information, conducting field studies, laboratory research, and protection of the health of Federal employees."

An added factor in the furtherance of industrial health activities is the provision in the Federal "Wage and Hour" Act of 1938 which forbids the employment of children under 16 or boys or girls of 16 or 17 at hazardous or unhealthful work. This provision of the act will necessitate some determination as to whether an occupation is or is not hazardous or unhealthful. The extension of social-security legislation and the participation of the Federal Government in industrial enterprises during World War II were additional factors in the development of governmental influence on industrial hygiene.

4. Role of the Chemist

While all this has been realized by public-spirited citizens and conscientious civil workers and much work has already been done, even more actual work for protection needs to be accomplished before one can feel that the problem has been adequately attacked. In this, the chemist should play a most important role. Chemists and chemical engineers should be part of the personnel of every industrial hygiene division, be it of a large industrial establishment, of a medical unit, or of a governmental arm. The plant chemist could well employ part of his time in work that would lead to the diminution and elimination of hazards.

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[11] R. R. Sayers and J. J. Bloomfield, "Industrial Hygiene Activities in the United States," *U. S. Pub. Health Service,* 1936.

The employer should realize that adequate industrial hygiene—the prevention, diminution, and elimination of industrial hazards and industrial poisoning—is of direct financial importance to him. He gains because of better work obtained, for the prevalence of fatigue is diminished. Less time is lost due to illness. Expenses caused by the need of medical care and hospitalization are reduced. The reduction in compensation losses alone is enormous. Sappington[12] notes that of the closed cases in the state of Wisconsin for 1936, "noxious dusts" with 71 cases accounted for only 6.6 per cent of the total number of cases of occupational disease disability indemnified during that year. However, the payment of compensation for these cases was $119,737.00, or 54 per cent of the total indemnity paid to the entire group.

Not only industry and commerce but every taxpayer, citizen, and consumer are affected by proper industrial hygiene, for in the last analysis the cost of every item and the governmental budget itself reflect the cost of compensation and the cost of care of the ill and the disabled. Not only does the individual worker gain from the adequate control of hazards and baneful substances but industry and commerce also profit.

The industrial hygiene chemist can aid in the diminution, elimination, prevention, and cure of hazards and poisoning by being able to detect industrial poisons in concentrations far below any quantity that can cause an injurious or toxic effect. The ability to do this implies, in general, the ability to keep such concentrations down to harmless levels.

Differentiation of Industrial Hygiene Chemist from Toxicologist

The role of the industrial hygiene chemist should be differentiated from that of the toxicologist. Toxicology is that department of pathology or medicine which deals with the nature and effects of poisons. The function of the toxicologist is to diagnose, detect, and estimate poisons in order to evaluate their forensic and medical importance. His work is generally limited to a particular victim or patient. Obviously a large part of his interest lies in the estimation of alkaloidal, drug, and food poisons and in detecting deliberate poisonings of a homicidal or suicidal nature or poisonings of an accidental or undetermined origin. The function of the industrial hygiene chemist is to detect and estimate poisonous, hazardous, and baneful materials used in industry and commerce. The chemical analyses of the hygiene chemist are used by the physician as an aid in diagnosis and proper therapy.

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[12] C. O. Sappington, *Medicolegal Phases of Occupational Diseases*, Industrial Health, Chicago, 1939.

The importance of the chemist employed for the purpose of the elimination of industrial hazards has another aspect not readily seen. Often the true hazard is not recognized until complete analysis has been made.

5. Scope of Analytical Chemistry as Applied to Industrial Poisons, Hazards, and Solvents

Whereas many other types of chemical analysis are fairly well delimited—as, for example, inorganic analysis, gas and air analysis, and anaylsis of metals and alloys—industrial hygiene chemistry covers a wider field. Hazards in industry cover the vast field of chemistry itself, for there are life and fire hazards in every branch of chemistry. Inorganic compounds and mixtures such as rocks, ores, and minerals; organic compounds such as benzene, aniline, and their derivatives; gases such as carbon monoxide, hydrogen sulfide, and methane; and metals such as lead, mercury, arsenic, chromium, and their compounds are all important chemical industrial poisons within the purview of the industrial hygiene chemist.

Not all industrial hazards are poisons in the strict sense of the word. Thus methane is a hazard because it may be present in sufficient quantity to be either an asphyxiant or a fire hazard. Industrial solvents such as the chlorinated hydrocarbons may not be fire hazards but they can be life hazards. In addition, the industrial hygiene chemist is often called upon to evaluate the potential hazard of known chemicals receiving greater utilization and new chemicals for which extensive use may be found in the future.

Harmful substances are not limited to a small number of industries. Thus, for example, lead is a hazard in over 150 industries; arsenic is a hazard in at least 50 industries; and benzene is a hazard in about 50 industries. The use of industrial solvents is steadily increasing. One may readily see that methods for a definite chemical hazard may be used in a large number of industries with but few modifications, involving sampling and the like, which are necessary because of the manufacturing process used in the particular industry. General methods for the detection and determination of industrial solvents and combustible vapors and gases are given in Chapter XII.

The number of occupational disease hazards encountered in an industry may be small, but many industries have a large number of industrial disease hazards. The one industry of tanning has as many as 42 occupational disease exposures,[13] many of which are of a chemical nature and among which may be mentioned exposure to hydrogen sulfide, hydrogen cyanide, arsenic, mercury, and chromium compounds.

6. Industrial Hazards and Poisons

Broadly speaking, the term occupational diseases includes a great variety of conditions arising from the use of harmful substances in connection with various trades and industries, and from exposure to unusual physical conditions, such as excessive heat, prolonged dampness, compressed air, radioactive air, repeated motion, pressure shock, and the like. These causes may conveniently be grouped as follows:[14]

(1) Mechanical
(2) Thermal
(3) Chemical
(4) Photic and radioactive
(5) Electrical
(6) Bacterial and parasitic (anthrax, glanders, etc.)
(7) Atmospheric (air compression, etc.)

Other terms used synonymously with occupational diseases are industrial diseases, diseases of dangerous trades, diseases of environment, maladies of professions, diseases of hazardous occupations, etc.[15,16] The associated diseases, especially those of the respiratory system, such as tuberculosis, pneumonia, chronic bronchitis and pleurisy, are also included by some authorities; for while not due primarily to the occupational hazard, they are sometimes the result of that hazard.

An industrial exposure is not necessarily an occupational disease hazard. The amount, kind, and length of exposure are the determining factors in most cases.

a. Definition of Industrial Disease

Briefly an industrial hazard is a substance or a condition that causes an occupational disease. Sappington[14] defines an industrial disease as one which occurs with characteristic frequency and regularity in occupations where there is a specific hazard as the cause that operates to produce effects in the human body recognized clinically by the medical profession as pathological changes and effects produced by the specific occupational hazard involved.

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[13] D. K. Minster, *J. Ind. Hyg.*, *7*, 299 (1925).

[14] C. O. Sappington, *Medicolegal Phases of Occupational Diseases*, Industrial Health, Chicago, 1939.

[15] C. T. Graham-Rogers, *Industrial Diseases Rapid Reference Manual*, N. Y. State Dept. Labor (1925).

[16] L. I. Dublin and R. J. Vane, *U. S. Bur. Labor Statistics, Bull. 582* (1933).

In this book we cannot be concerned with the conditions of exposure to excessive heat, prolonged dampness, compressed air, infective material such as hides, rags, or wool, or electrical causes, for these conditions are only indirectly concerned with analytical chemistry as applied to industrial hazards.

Definition of Industrial Poison. Dr. Thomas M. Legge, a British authority on industrial hygiene, defines an industrial poison[17] not only as a substance which acts chemically and effects transient or permanent injury to the tissues, organs, or functions of the body but also as one that is employed, produced, or somehow occasioned in an industrial occupation and that is brought about (in the absence of sufficient precaution) inadvertently and consequently against the will of the person poisoned.

As a more general definition of a poison, we may use that of Sollmann:[18,19] A poison is any substance, which, acting directly through its inherent chemical properties and by its ordinary action, is capable of destroying life or of seriously endangering health when it is applied to the body, externally or in moderate doses (to 50 g.) internally.

McNally[20] defines a poison as a substance that, introduced into or upon the body and absorbed into the blood stream, and acting chemically, is capable of seriously affecting health or destroying life.

It is clear from these definitions and that of Sappington's of an industrial disease that an industrial poison is one which produces its harmful effects as a result of repeated exposures or long exposure to even small concentrations of a substance that is not harmful in those small concentrations taken as one dose or inhaled for a short time.

b. Classification of Industrial Poisons

Classification of industrial poisons may be attempted by dividing them into their physical states, viz., gases, liquids, and solids. In order to see how these physical states apply, we must realize that these are the three states in which chemical industrial poisons and hazards may be taken into the body, namely: (1) as gases or vapors, (2) as liquids, and (3) as solid substances or dust.

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[17] T. M. Legge, *J. Ind. Hyg.*, *2*, 121 (1920).

[18] T. Sollmann, *A Manual of Pharmacology*, Saunders, Philadelphia, 1944.

[19] R. R. Sayers, *U. S. Pub. Health Repts.*, *53*, 217 (1938).

[20] W. D. McNally, *Toxicology*, Industrial Medicine, Chicago, 1937.

There are, moreover, three main channels through which these baneful materials can enter the human system and they are:

(a) Breathing into the respiratory tract, as dust, fumes, vapors, mists, or gases
(b) Swallowing with saliva, water, or food into the digestive tract
(c) Absorption through the skin

An example of (a) is the breathing of dust in mine drilling or quarrying, or the breathing of benzene during the use of rubber cement. An example of (b) is the sucking of brushes dipped in radioactive paint. An example of (c) is the absorption of hydrogen cyanide gas through the skin.

While the above-mentioned means of entrance may be considered the normal modes of entrance into the system, it is necessary to include a fourth type, accidental entrance of industrial poisons. This type includes a miscellaneous grouping such as absorption through cuts into the flesh or irritation of the skin and entrance through the ears and eyes.

The toxicologist classifies poisons into four main groups: (1) metallic poisons, (2) volatile poisons, (3) alkaloidal poisons, and (4) nonalkaloidal poisons. He does so mainly because in many instances he may not know what the poison is and so must isolate and classify it before identification. The industrial hygiene chemist in most instances knows the identity of the hazard and is mainly interested in how much of the baneful substance is present, and where it may be located.

For purposes of clarity and for the purposes this book is designed to serve, harmful substances, industrial poisons, and hazards may better be classified as inorganic or organic chemical substances. These two basic groups may be further subdivided for analytical purposes, the former into metallic and nonmetallic substances and the latter into the main organic chemical groups. The methods of analysis of these substances will, consequently, fall into one or another of these group types of analysis.

c. Effects of Industrial Poisons

The effect produced in and on the human body by specific industrial poisons will be discussed in the sections devoted to the methods for the analysis of that harmful substance. The damage arising from the inhalation, swallowing, or absorption of an industrial poison may be either local or remote, and depends upon whether the material is a protoplasmic poison, whether it is caustic in reaction, or whether it is absorbed into the blood stream and carried to other centers that are in turn affected.[21,22]

Briefly, the effects of industrial hazards and their causes may be summarized as follows:[23]

(1) Irritation of the mucous membranes—chlorine, nitrous fumes, sulfur dioxide, formaldehyde, and others.

(2) Alteration of the components of the blood—this effect is peculiarly the property of nitro and amino derivatives of benzene, arsine, and carbon monoxide. Greenburg[24] and his co-workers state that the glycols belong to this group.

(3) Action on the brain and nervous system—carbon disulfide and unsaturated carbon compounds.

(4) Remote action on the metabolism, by action on organs and tissues—lead, phosphorus, tetrachloroethane, benzene, toluene, and their nitro derivatives.

(5) Action on the respiratory tract, such as action on the lungs—silica and asbestos dust.

Chemists are interested in the effects and symptoms of industrial poisoning because they are in immediate contact and control where poisonings of this nature are liable to occur. A physician is unlikely to see a case until it is too late to remedy or alter the industrial condition.[25]

Sayers, DallaValle, and Yant[26] summarize more fully the effects of industrial poisons on the body.

Action of Air-Borne Contaminants on the Body. The actions of such substances upon the body differ widely, but in general they may have the following effects:

(1) They may cause skin irritation, or dermatosis, or affect the mucous membranes of the respiratory tract and eyes. This is true of acid vapors and certain caustic compounds easily distributed into the air.

(2) They may enter the lungs or be absorbed by the blood stream and produce systemic poisoning. Such substances as benzene vapors and lead fumes or dust are typical examples. Substances in this group may have their action on the blood, on the nervous system, or on the other body tissues, and may produce deleterious effects when the exposure is severe or prolonged.

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[21] L. T. Fairhall, *J. Ind. Hyg. Toxicol.*, *18*, 669 (1936).

[22] R. R. Sayers, *U. S. Pub. Health Repts.*, *53*, 217 (1938).

[23] T. M. Legge, *J. Ind. Hyg.*, *2*, 293 (1921).

[24] L. Greenburg, M. R. Mayers, L. Goldwater, W. J. Burke, and S. Moskowitz, *J. Ind. Hyg. Toxicol.*, *20*, 134 (1938); *N. Y. State Ind. Bull.*, *17*, 269 (1938).

[25] Y. Henderson and H. W. Haggard, *Noxious Gases*, Reinhold, New York, 1927.

[26] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem.*, *26*, 1251 (1934).

(3) They may produce asphyxia directly or indirectly, as in the case of excessive amounts of hydrogen cyanide, hydrogen sulfide, or carbon monoxide. The action of these gases is varied. They may affect the respiratory center or the nerve endings in the lungs, causing a cessation of breathing, or, as in the case of carbon monoxide, so combine with the hemoglobin of the blood that oxygen cannot be furnished the tissues.

(4) They may, as in the case of certain dusts such as silica, granite, and asbestos, cause a fibrosis of the lung tissue which predisposes to tuberculosis.

(5) They may exhibit a combination of the above effects. Some substances, such as nitrobenzene, not only cause a dermatosis when in contact with the skin but may also act as systemic poisons.

(6) They may produce no demonstrable effects on prolonged exposure. This is particularly true of cotton and some wood dusts.

Skin Affections. Industrial skin affections according to available statistics account for the largest number of occupational disease claims of any one group of causes.[27] Occupational dermatergoses have been classified by White[28,29] and Schwartz.[30]

Acute and Chronic Poisoning. Industrial poisoning is of two main types, acute and chronic. The first is induced by large or relatively massive doses of a poisonous or baneful substance. The latter is the result of repeated small doses. Thus, for instance, acute poisoning from carbon tetrachloride vapors does not result until an exposure to a concentration of 1,000 to 1,500 parts per million for 30 minutes. A concentration below this amount is, however, by no means a safe level. Continuous exposure to concentrations but slightly higher than 100 parts per million will cause serious physiological disturbances.[31]

Though the effects of acute poisoning are more readily apparent, the deep-seated effects of slow and chronic poisoning are often much more damaging. The chances of recovery from acute poisoning, if it is not lethal, are greater than from chronic poisoning.

From the viewpoint of the industrial-hygiene chemist, the conditions causing chronic poisoning are far more significant than those causing acute poisoning. Acute poisoning is more often likely to be accidental in nature and thus falls within the scope of the toxicologist, whereas chronic poisoning is generally the result of some industrial or manufacturing condition and therefore is distinctly a problem for the industrial-hygiene chemist.

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[27] C. O. Sappington, *Medicolegal Phases of Occupational Diseases,* Industrial Health, Chicago, 1939.

[28] R. P. White, *J. Ind. Hyg., 8,* 367 (1926).

[29] R. P. White, *Dermatergoses,* Lewis, London, 1934.

[30] L. Schwartz, *U. S. Health Service, Bull., 215* (1934); *229* (1936); *249* (1939).

[31] H. F. Smyth, H. F. Smyth, Jr., and C. P. Carpenter, *J. Ind. Hyg. Toxicol., 18,* 277 (1936).

7. *Air Pollution*

The importance of air pollution on the health of a community was brought sharply into focus by the Donora, Pa. "disaster" in October 1948. The deaths of a number of persons and the illness of many persons were attributed to a smog or fog which was unusually heavy and settled over the town for a period of about 4 days. There were 500 cases of illness and 19 deaths reported in the period from 1:00 a.m. Saturday, October 30 to 1:00 p.m. Sunday, October 31, 1948 in a total population of 14,000 people.[31a]

In this city there is a zinc smelting plant, a shoe factory, and a slag crushing plant. Some steel mills are located a distance away. No conclusions as to the cause of these illnesses or deaths were definitely drawn since no analyses of the air were made during the actual period of the smog but many were convinced that they were due to the discharge of the zinc smelting plant stacks. There were, however, only 9 cases of illness and no deaths reported at the zinc works.

Analyses of sulfur dioxide made shortly after most of the fog had lifted indicated a concentration of 0.54 part of sulfur dioxide per million parts of air at 6:23 a.m. and 0.08 part per million at 1:20 p.m. on Sunday. These data extrapolated to Saturday indicated a concentration of 1 part per million. Sulfate concentrations were found to be low and fluorine determinations were made but the results indicated the fluorine content to be very low.

Johnstone,[31b] in a study of the Los Angeles smog problem, points out that a concentration of sulfur dioxide exceeding 1.0 part per million at the ground is considered excessive and damaging if allowed to continue for a few hours.

In an analogous problem which occurred in Belgium in 1935 in which about 60 deaths were reported, the deaths and illness were attributed to sulfur dioxide and sulfur trioxide, but Flury came to the conclusion, in an investigation made after the occurrence, that this was unlikely and that it was more probable that fluorine compounds were the cause.

[31a] J. Shilen, Joint Meeting of New York, New Jersey, and Pennsylvania Sections Am. Ind. Hyg. Assoc. Meeting, Dec. 1948.

[31b] H. F. Johnstone, *J. Ind. Hyg. Toxicol.*, *30*, 358 (1948).

Much of the analytical chemistry of industrial hazards deals with the estimation of substances in air, for while there are three or four channels through which chemical poisons can enter the body, the chief portals of entry are the respiratory tract and the skin. The swallowing of industrial poisons can be prevented almost at will. Absorption through the skin, except where it is a matter of contact with a chemical agent, is again a question of the chemical contaminant being in the air. Accidental entrance cannot be considered. Hence methods for the estimation of contaminants in the surrounding air will form a most important part of this book. There is, however, an essential difference between industrial-hazard air analysis and customary gas analysis. In the usual type of air or gas analysis, the analyst is concerned with the percentage composition of the air or gas as a whole. In the analytical chemistry of industrial hazards, the analyst is interested in the contaminants and noxious materials in the air and not in the actual composition of the air. Since these industrial poisons are usually only a very small portion of the composition of the air to be analyzed, the ordinary methods of air analysis are not applicable.

Because these methods do deal with air, they are not at all limited to factory, shop, garage, mine, or quarry, but are equally applicable to the study of air pollution and air sanitation. The sampling instruments and methods used are in many instances identical. Indeed the American Public Health Association delegates its committee on Ventilation and Atmospheric Pollution to a sub-section of the major Division of Industrial Hygiene.

Smoke Abatement

Smoke and fumes are the most significant factors in air pollution, acid gases are next in importance, while factors such as pollen, yeasts, and bacterial contamination are least important. Air pollution is almost synonymous with "smoke abatement."[32]

The losses attributable to smoke are large and may be classified as follows: economic losses because of imperfect combustion of fuels; extra expense in cleaning clothes; losses resulting from disfigurement of residences, offices, buildings, and factories, with additional loss charged to repainting, etc.; losses assigned to soiled merchandise in stores; injuries to grass, shrubs, and trees bordering the streets and in parks; loss of daylight and ultraviolet light; and the possible injurious effects on health.[33]

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[32] S. Pincus and A. C. Stern, *Am. J. Pub. Health, 27,* 321 (1937).

[33] *U. S. Pub. Health Repts., 51,* 15 (1936).

The principal source of air pollution is the combustion of fuel,[34] not only that used for heating purposes but also that used in internal combustion engines. These engines emit exhaust fumes which are malodorous, cause nausea, headache, and, if the concentrations of the noxious components of the exhaust fumes are high enough, death.

Pincus and his co-workers calculate that during a typical year there is discharged into the atmosphere of New York City, exclusive of the discharge of internal combustion engines, 300,000 tons of soot, tar, cinders, and fly ash; and 350,000 tons of sulfur, which probably forms 1,000,000 tons of sulfuric acid. The analyses of these investigators consisted mainly of the determination of two fractions of soluble and insoluble solid contaminants of the air. In the former, total soluble solids, ammonia, sulfur trioxide, chloride, and ash content were estimated. In the latter, total insoluble solids, ash, carbon, and tar contents were ascertained. In addition estimation of the sulfur dioxide and carbon monoxide content of the air was also made.

8. *Error and Accuracy*

The subject of error and accuracy presents a somewhat different aspect in the field of industrial hazards. Purists in analytical chemistry might be horrified by the latitude permitted in some types of industrial-hygiene analysis. It is indeed true that every measurement entails some error. Hence to work far outside the limits of that error is to involve useless labor with no gain in accuracy. The accuracy of the final result is quantitatively governed by the accuracy of the least accurate measurement.

In the field of analytical chemistry as applied to industrial hazards, we encounter substances which are toxic in minute quantities. Our methods must, naturally, be sufficiently accurate to enable us to detect and estimate these minute quantities. The methods must be more than sufficiently sensitive to detect the toxic threshold of a noxious material. Once, however, the threshold of toxic concentration is reached and passed, it really matters little how accurate the analysis is. The method must in such cases be accurate enough to warn of the danger and to disclose the degree of danger. Thus, for example, Lehmann[35,36] found that 0.015 g. per liter (4,700 parts per million) of benzene produces listlessness and confusion after half an hour, and that 0.02 to 0.03 g. per liter (6,260 to 9,390 parts per million) for a few hours may cause loss of consciousness. For the purposes of accuracy as far as the analysis of benzene in this instance is concerned, it is not significant whether 90 or 100 parts per million of benzene is present in the air, but rather whether there are 50, 100, 200, 300, 500, 1,000, etc., parts per million present. We are more interested in the relative amount of benzene vapor in the air, expressed in round numbers rather than in the precise amount present. Furthermore, when one considers that, under plant conditions, particularly in the summer season when windows are open and natural ventilation is good, the benzene vapor concentration in workrooms is subject to large and almost continuous variations, errors of as much as 10 per cent are not of serious consequence.

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[34] J. Siegel and B. Feiner, *Heating, Piping, Air Conditioning, 17*, 495, 557 (1945).

[35] K. B. Lehmann, *Arch. Hyg., 75*, 1 (1911–1912).

[36] L. Greenburg, *U. S. Pub. Health Service, Reprint 1096* (1926).

Practically speaking, the same conditions hold for the accuracy to be expected in all analyses. A method to be valuable in the field of the analytical chemistry of industrial hazards must be sufficiently accurate to *detect* and thus to warn of danger and to disclose the *degree* of hazard. Tables 3, 4, 5, 6, and 7 (Appendix) give information on limits of toxicity and the toxic threshold of a number of industrial hazards.

Effort to obtain accuracy greater than that which is necessary to give the needed and useful information is impractical.

Throughout the text more than one procedure is often detailed for any particular determination. This is done intentionally, for the analyst is wont to find one method preferable to another. Furthermore, in the opinion of the author, check results obtained by different methods are more indicative of the true estimation than check results obtained by the same method. References to still other methods are given in the bibliography appended to each chapter.

There is, however, one other aspect of industrial-hygiene analyses that King[36a] stresses. Most of the toxicological thought of industrial-hygiene chemistry has been oriented toward continuous exposure during the working day. In aviation there exists the possibility of exposures to very high concentrations for a relatively short time. There is little data that has been gathered from this point of view, that is, data concerning adequate tolerances for short time-high concentration exposures. It will be found that some of the methods in this text are designed for the purpose of obtaining such information.

The more important industrial hazards, from the point of view of number of workers injured and number of industries in which they are hazards, are treated more fully than those which do not have the same importance. Among these might be mentioned carbon monoxide, lead, arsenic, mercury, benzene, chlorinated hydrocarbons, free silica, and dust.

[36a] B. G. King, Greater New York Safety Council Convention, New York, 1949.

A survey made by the U. S. Public Health Service[37] showed that approximately 1,500,000 workers in the United States are exposed to carbon monoxide; 800,000 persons handle lead and its compounds; 34,000 are exposed to arsenic and its compounds; nearly 33,000 handle mercury and mercury products; somewhat more than 1,000,000 persons are exposed to the inhalation of silica dust and 1,500,000 more are exposed to silicate dust; more than 750,000 workers are exposed to organic solvents, while some 30,000 may inhale benzene vapors. These few figures, more of which may be obtained in the references cited, indicate the vastness of the industrial hygiene problem.

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[37] J. J. Bloomfield, V. M. Trasko, R. R. Sayers, R. T. Page, and M. F. Peyton, *U. S. Pub. Health Service, Bull. 259* (1940).

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CHAPTER II

Sampling

1. Precision of Sampling

In order to make a correct analysis, a proper, representative, and adequate sample of the material to be analyzed must be obtained. Very likely there are as many incorrect determinations resulting from improper sampling as from the combined errors of manipulation, measurement, and calculation. An improper sample makes a subsequent analysis practically worthless. No analysis can be better than the sample nor can the chemist improve the quality of the sample. Sampling is as important in the field of the analytical chemistry of industrial hazards as it is in other fields. This importance is never to be underestimated for often comfort, illness, and even life itself depend upon an accurate estimation of the noxious components of a sample presumed to be accurately obtained.

Sampling of industrial poisons is often beset with more and greater difficulties than the sampling of other materials. Thus, it becomes a serious problem to sample the air that a workman breathes at the point that he breathes it for a partial or entire working period. Various devices and attempts have been made to overcome this difficulty. These will be discussed in the text. At times, it is important to sample in relatively inaccessible places, such as the blisters of a warship, a manhole, a sewer, or a mine. One can readily see the numerous difficulties involved.

The material to be sampled may be the noxious substance itself or it may be a mixture of which the poison is a component. In any event it will be, as explained in Chapter I, either solid, liquid, or gaseous. The times that it is necessary to sample solids or liquids are reserved, in the main, to obtaining samples which will yield information concerning the composition of the material the workmen handle. If it is merely desired to obtain some idea of the constituents or components qualitatively, rather than to make a precise determination of the exact percentage composition, then it may be sufficient to scrape the settled dust off a rafter or beam of a shop or out of a ventilation duct or flue, or to take a random sample of raw material or finished product from a warehouse, or to take some portion of a plating bath or a sample from a collector bin.

The sample so obtained is then subjected to analysis by the usual gravimetric, titrimetric, colorimetric, etc., methods.

Where it is necessary to obtain the exact percentage composition of raw materials or of settled dust or other solid or liquid material, sampling should be performed by the standard customary methods. For instance, for bags or boxes of ground raw materials or finished products, or for such substances in a collector bin, a sampling tube, trier, or scoop may be used. Liquid substances, which form a most important group of industrial hazards, may be sampled with a thief or ladle. Products in smaller subdivisions, such as cans of paint, may be sampled by taking sufficient cans to make a representative sample from a given lot number. The sampling of gaseous materials will be discussed fully in subsequent sections. A method for sampling rock in a quarry is described in Section 3 of Chapter VI.

2. *Sampling Instruments*

Various implements have been developed to assist in the proper sampling of solid and liquid substances. The more important of these are the sampling tube, the trier, the scoop, and the thief. The *sampling tube* (Fig. 1) is an instrument designed for the sampling of powders. It is generally a brass tube, 2 to 3 feet long and $1/2$ to 1 inch wide, with a conical sharp tip at one end and a handle at the other. The tube has a slot which extends almost the entire length of the sampling device from the tip to the handle. Some of these instruments consist of two brass telescopic tubes having slots which may be opened and closed by rotation of the inner tube. The outer tube is equipped, as was described above, with a conical tip and handle. The sharp tip enables the instrument to penetrate the material being sampled.

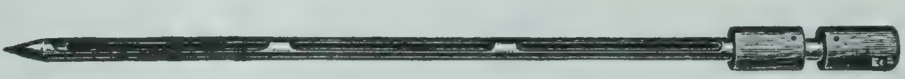

Fig. 1. Sampling tube. (*Courtesy Eimer and Amend*)

The *sampling trier* (Fig. 2) is a very long gouge. It has about the same dimensions as the sampling tube. The tip and edges of the trier are sharpened so that after insertion into the material to be sampled, turning the trier will cut a core of the material. The general method of use of either the trier or sampling tube is to insert the instrument practically its full length into the material being sampled from a point near a top edge or corner, through the center, to a point diagonally opposite the point of entry. Usually two or more cores are withdrawn from points equidistant from the first.

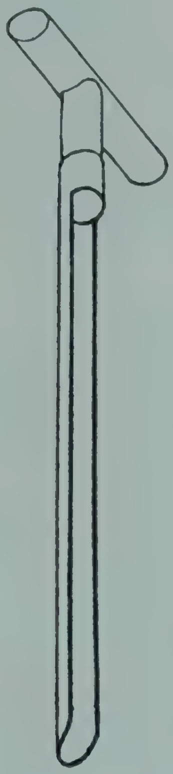

Fig. 2. Sampling trier.

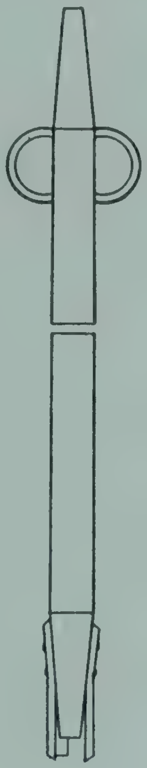

Fig. 3. Oil thief.

The *thief* is an instrument which is used for sampling liquids. It is a tube, generally about 2 or 3 feet long, which has holes in a cap at the bottom end. The tube is inserted into the liquid and when the solvent has risen to the same level as the surrounding liquid, the tube is closed by pushing the cap against the bottom of the container. The thief is then withdrawn and the sample is transferred to a sample bottle. A variation of this type of thief is the oil thief (Fig. 3), which is a copper tube about 3 feet long and $1^{1}/_{4}$ inches in diameter, with cone shaped ends having an opening $^{3}/_{8}$ inch in diameter. Three legs are placed on the lower end to hold the opening $^{1}/_{8}$ inch from the bottom of the drum. Two rings, soldered to opposite sides at the upper end, permit holding the thief with two fingers, leaving the thumb free to close the upper opening and thus withdraw the sample.

The U. S. Bureau of Mines[1,2] uses the "scoop and brush" method of collecting settled dust samples. A metal scoop, 6 inches wide, a 3-inch paint brush, a sizing screen, and a piece of oilcloth comprise the outfit.

After the sample has been withdrawn or taken with one of these instruments or even by simpler methods, such as by the use of a ladle or dipper in the case of liquids or in the case of solids by a shovel, it must be transferred to a proper sample bottle, jar, or container. If the liquid is a solvent, care must be taken not to place it in a container which has some part soluble in the solvent. Thus if benzene is being sampled, the sample should not be placed in a rubber stoppered container or one which has a rubber gasket.

All containers should be properly labeled, giving the date of sampling, the time, if necessary, the place, and the type of sample. The container should be sealed in such a way that the contents cannot be tampered with nor the contents leak or spill. Metal sampling instruments should not be used with corrosive materials unless adequately protected.

3. Basic Methods of Air and Gas Sampling

The proper sampling of air for the examination of noxious substances, dust, etc., presents greater difficulties than does the sampling of solids and liquids. It is often necessary not only to obtain a sample of air but to obtain it in a particular spot at a particular time. It may be necessary to take a sample right near a worker's nose or mouth, or near or within an exhaust duct. You may recall the example given in Chapter I concerning the variation in concentration of carbon monoxide from the exhaust of an automobile near the exhaust and at a distance of 30 feet. The same sampling problem exists for many industrial poisons.

In general, samples must be taken with a particular purpose in mind. Not only is the position at which the sample is taken of importance—namely, whether it is to represent the locale of the worker, the average workroom atmosphere, or the source of the contaminant—but the time of exposure of the worker also must be considered.

For the purposes of the analytical chemistry of industrial hazards, there are two basic methods of sampling air and gases. The first method is to obtain a definite volume of air within a gas collector, at a known

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[1] C. W. Owings, *U. S. Bur. Mines, Inform. Circ. 6129* (1929).

[2] C. W. Owings, W. A. Selvig, and H. P. Greenwald, *U. S. Bur. Mines, Inform. Circ. 7113* (1940).

pressure and temperature, in a manner entirely analogous to the sampling of gases.[3] This sample is then taken to the laboratory to be analyzed or is analyzed in the field.

The second basic method is to pass a known volume of air or gas through an absorbing medium or solution or equivalent means. The noxious material or contaminant is thus absorbed or adsorbed, and the absorbing or adsorbing medium or agent is subsequently subjected to analysis either in the field or preferably in the laboratory. Where the gross components of a gas or of air are to be estimated, the first basic method may be used; where a small or minute amount of a contaminant is to be estimated, the second basic sampling method is to be preferred.

Where a definite volume of gas is required or desired as the sample to be analyzed, there are two possible types of sample that may be taken. These are known as "instantaneous" (also known as "grab," "spot," and "snap") samples and "continuous" samples. Instantaneous samples are those taken at a particular time and place within an interval of a few seconds to a minute or two and they represent the composition of the air or gas at that time and location. They are most often taken with evacuated bottles or gas collectors, although they may be taken with liquid displacement devices.

Continuous samples are taken where a comparatively large volume of gas must be sampled or where the composition of the air being sampled is not uniform. In the former case, it is necessary to pass the air or gas through some absorbing agent in order to trap the contaminant to be estimated. In the latter instance, a sample taken continuously for a given period of time will give the average composition, as explained in the section describing gas or liquid displacement collectors for continuous sampling (Section 4d). It may be preferable, if the composition of the gas or air is not uniform, to take several grab samples at different times and locations rather than to take one continuous sample.

It has been recommended that samples be collected in at least three general sampling locations in order to get a fairly complete sample of the environment of a worker as follows:[4]

(1) In the immediate vicinity of the workers in a particular environment
(2) Near the source of the contaminant entering the general atmosphere
(3) The general workroom atmosphere

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[3] W. P. Yant and L. B. Berger, *U. S. Bur. Mines, Miners' Circ. 34* (1936).

[4] *Report of Sub-committee on Chemical Methods in Air Analysis. Sampling and Sampling Devices, Am. Pub. Health Assoc., Yearbook 1939–40,* p. 92.

It is not always possible to obtain all of these types of samples. It is important to bear in mind the type of sample obtained and not to generalize or average results indiscriminately. Only similar types of samples may be justifiably compared.

It is well to note that where one of the noxious components to be estimated is a highly reactive substance, as, for instance, sulfur dioxide, or hydrogen sulfide, or nitrogen tetroxide, and the atmosphere is sampled by means of a gas collector, it is preferable to make the analysis directly in the field; for by the time the gas collector gets to the laboratory, the noxious component may have reacted completely with the container itself. A moderately accurate field test is better than a totally inaccurate laboratory analysis.

The devices and methods used in the sampling of dust and dust-borne contaminants will be described and detailed in Chapter V.

4. *Gas Sample Containers and Collectors*

In order to obtain a sample of gas or air by either of these basic methods, the air containing the contaminant must be placed in a sample container or collector or must be, as was previously explained, passed through some absorbing medium by some device. Sample collectors and containers may be classified as follows:

Vacuum tubes
Vacuum bottles
Gas- or liquid-displacement tubes
Gas- or liquid-displacement tubes for continuous sampling
Metal-type containers
Glass bottles
Syringes
Traps, bubblers, and absorbers.

Each of these types of gas collectors lends itself to some special means of sampling.

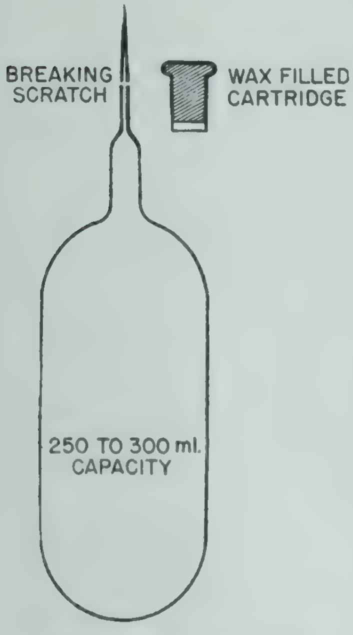

Fig. 4. Vacuum-tube sample collector.

a. Vacuum Tubes

Vacuum tubes (Fig. 4) are strong glass bulbs from which 99.97 per cent or more of the air has been removed by a vacuum pump and the necks of which have been hermetically sealed by heating and drawing during the final stage of evacuation. For the analysis of the gross components of air or of mine gases, vacuum bulbs with a capacity of 250 to 300 ml. are sufficient. For the analysis of air or gases in which ingredients of low concentration are being estimated, as for instance in the determination of carbon monoxide larger bulbs of about 1,000-ml. capacity may be used. The glass must be sufficiently strong to withstand the atmospheric pressure of 13 to 14 pounds per square inch, for the internal pressure of the vaccum tube is practically zero.

In use, the ampoule-like drawn-out end is scratched and broken. The air rushes in to fill the vacuum until the internal pressure equals the external pressure. Then the broken end is sealed with a ball of wax or with a wax-filled cartridge, shown in Figure 20. The bulb may now be shipped to a laboratory for analysis. One can see that for practical considerations vacuum tubes are used almost exclusively for grab samples.

These sample containers are recommended by the U. S. Bureau of Mines for all samples of mine air taken for shipment to its gas laboratory at the Pittsburgh Experiment Station. They have the advantage of being very simple to use, as neither pumps nor evacuating devices are needed at the point of sampling. No manometer need be attached, for the pressure of the sample is taken as the barometric reading. Because of its simplicity of use, field men and workmen may be trained to do the sampling. Its disadvantage lies in the fact that the tube must be re-evacuated, redrawn, and resealed to be used again.

b. Vacuum Bottles

Generally bottles or flasks with strong walls are used. They are fitted with a two-hole rubber stopper. One hole is equipped with a thermometer and the other contains a T tube fitted with two stopcocks and attached to a manometer. The bottle is evacuated by opening stopcock *a* by means of some evacuating device such as a suction pump. Then stopcock *a* is closed and stopcock *b* is opened. The pressure registered by the manometer and the temperature shown by the thermometer are recorded. Stopcock *b* is then closed. The tube arm with stopcock *a* is connected with the source to be sampled and then it is opened. When equilibrium has been established, stopcock *a* is closed and stopcock *b* is again opened. The pressure indicated by the manometer and the temperature indicated by the thermometer are again noted. The amount of gas or air taken into the bottle may then be computed as directed on page 75. The bottle may then be quickly sealed with rubber stoppers, bakelite screw caps, etc., or if the analysis is to be made near the point of sampling, the stopcocks may merely be closed and the manometer disconnected. Collector tubes may be handled in an entirely analogous manner.

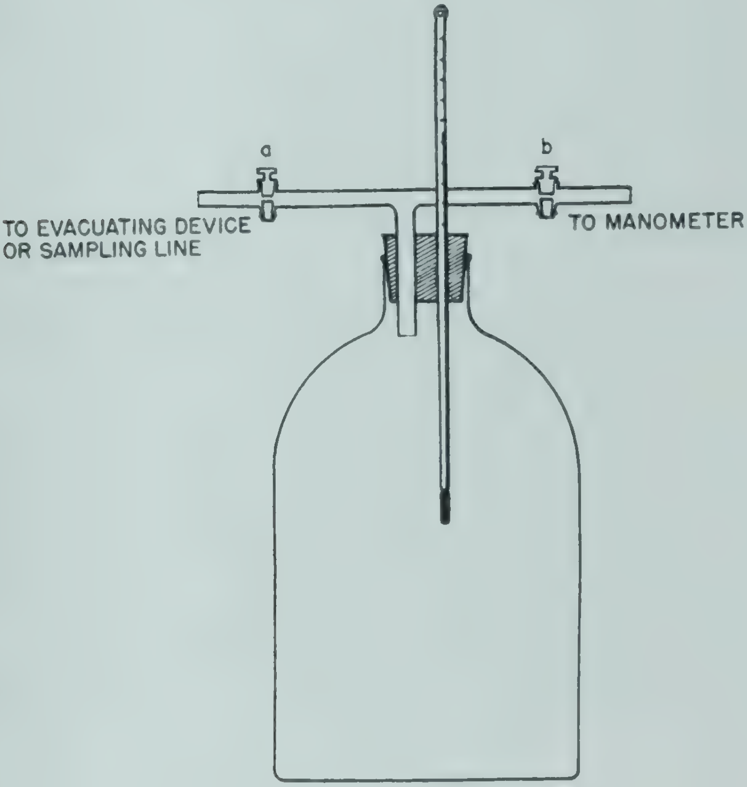

Fig. 5. Vacuum-bottle sampling.

Alternative vacuum bottle collectors are illustrated in Figures 5A and 5B. These collectors[5] have been designed for sampling atmospheres containing contaminants that are not readily trapped in absorbing solutions or on adsorbents. The bottles are evacuated and then are sealed by giving the cap a half turn. To take the sample the cap is turned to the open position at the spot to be sampled. After being filled with the air sample, reagents such as 10 ml. of dilute sulfuric acid and a few drops of hydrogen peroxide may be added in a nitrogen oxide determination or 10 ml. of nitrating acid in the case of a benzene determination.

The Shepherd bottle has great versatility. It can be used as a "universal" sampling flask. Thus it can be used for sampling (1) by evacuating it, (2) by aspirating after inserting a glass tube, (3) by displacing a liquid, and (4) as a bubbler using an adapter head. The flask may subsequently be used for operations such as boiling or distillation, and as originally designed may be attached to a Shepherd gas burette with sufficient sample for triplicate determinations.

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[5] Martin Shepherd, U. S. National Bureau of Standards, Washington, D. C.

c. Gas- or Liquid-Displacement Collectors

These gas collectors are of various designs, some of which are shown in Figure 6. They are satisfactory and adequate if analysis is to be made shortly after sampling or within a few days of sampling. The simplest of these devices is a glass bulb of about 250-ml. capacity with two end tubes suitable for closing with heavy rubber tubing and screw clamps. Short pieces of glass rod or glass plugs may be used instead of the screw clamps, but they must make a tight fit with the rubber tubing and they should be pushed up to make a flush contact with the end of the tube of the sampling collector.

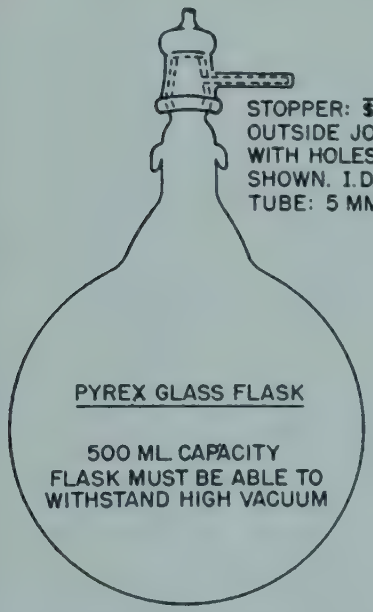
STOPPER: ₮ 14/20
OUTSIDE JOINT,
WITH HOLES AS
SHOWN. I.D. OF GLASS
TUBE: 5 MM.
PYREX GLASS FLASK
500 ML. CAPACITY
FLASK MUST BE ABLE TO
WITHSTAND HIGH VACUUM

Fig. 5A. Vacuum bottle collector, rotating-cap type.

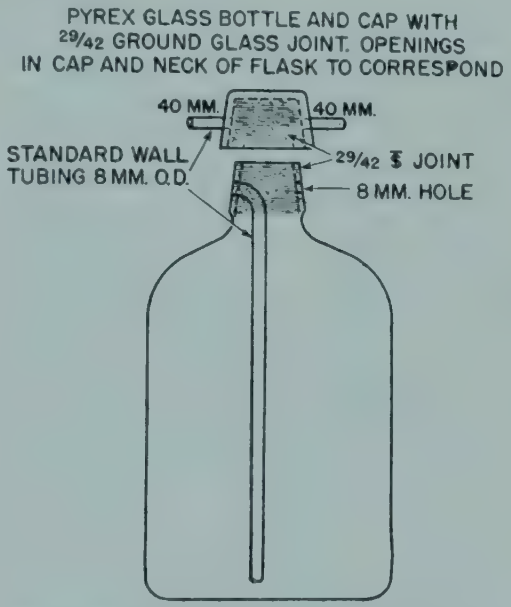
PYREX GLASS BOTTLE AND CAP WITH
29/42 GROUND GLASS JOINT. OPENINGS
IN CAP AND NECK OF FLASK TO CORRESPOND
40 MM.
40 MM.
STANDARD WALL
TUBING 8 MM. O.D.
29/42 ₮ JOINT
8 MM. HOLE

Fig. 5B. Gas-sampling bottle standard 500-ml., rotating-cap type.

Better than the container just described is the gas collector fitted with stopcocks instead of the tubes to be sealed with rubber tubing and screw clamps. These are furnished by many firms handling chemical laboratory equipment. Those in which the stopcocks are joined very close to the body of the bulb, so that there is practically no stem between the body and the stopcock, are considerably less apt to be broken.

A variation of this type of gas collector is the separatory funnel. Various chemists have used small and large separatory funnels as gas-displacement collectors.[6,7]

Another type of gas- or liquid-displacement gas collector is the one (Fig. 7) equipped with two three-way stopcocks and two tubulatures at each end. These tubulatures may be of different bores to suit the flow of gas through the upper stopcock and the flow of liquid through the lower stopcock. By means of the extra tube, this type of collector permits the flushing of the sampling line either with the material to be sampled itself or with a confining fluid at the time of drawing the sample. This type also provides for the displacement of air from the tubing which connects the leveling bulb of an analytical device or measuring device to the collector.

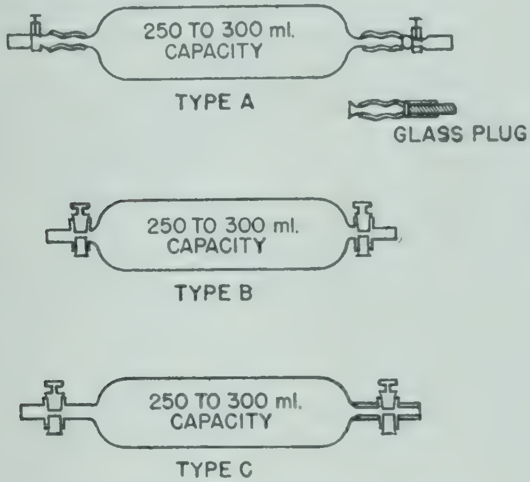

Fig. 6. Gas-sample collectors, gas- or liquid-displacement type.

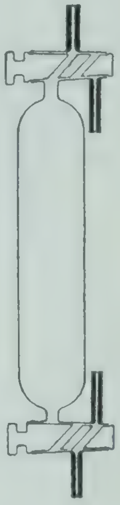

Fig. 7. Gas collector.

d. Gas- or Liquid-Displacement Collectors for Continuous Sampling

These gas collectors are very similar to those described in the previous section. They are fitted with stopcocks of the two-, three-way type (Fig. 8). However, they are generally equipped with an inner tube and the rate at which the sample is to be taken can be controlled by the distance between the end of the inner tube and the end of the tube tap.[8] The bore

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[6] J. Siegel and W. J. Burke, *N. Y. State Ind. Bull. 18,* 17 (1939).

[7] W. D. McNally, *Toxicology,* Industrial Medicine, Chicago, 1937.

[8] G. N. Huntly, *J. Soc. Chem. Ind., 29,* 312 (1910).

of the tube taps may also be used to regulate the flow, as may the length of the tube. If necessary an extra piece of tubing may be sealed on in order to increase the length of the exit tube.

The inner tube prevents sucking back or backward diffusion of the sampled gas. However, the rate of sampling may be controlled by using a sample collector without the internal tube by arranging the exit tap of the gas collector so that it will dip into a vessel of such a shape that the rate of outflow decreases as the pressure of the gas increases.[9] In another device the sample of gas is drawn into the collector by a filter pump at a rate controlled by a counterpoise.[10]

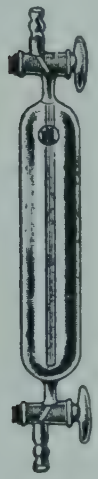

Fig. 8. Inner-tube sampling collector.

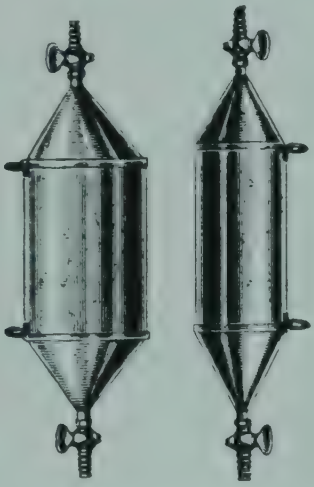

Fig. 9. Metal-type gas collectors.

(Courtesy Will Corporation)

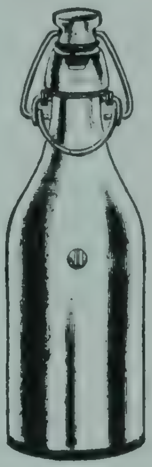

Fig. 10. Magnesia-bottle collector.

e. Metal-Type Gas Collectors

Metal-type gas collectors (Fig. 9) are analogous to the gas- or liquid-displacement collectors described in the preceding paragraphs. They have the advantage that they are practically nonbreakable and are readily available from laboratory-equipment concerns. On the other hand, this type of container is likely to rust or react with the oxygen in the collector. They cannot be used for sampling air or gases containing hydrogen sulfide, sulfur dioxide, or nitrogen tetroxide, as these gases will react with the metal container. If this type of gas sample collector is used, the analysis should be made as soon as possible after sampling. If it is neces-

[9] G. Lunge and H. R. Ambler, *Technical Gas Analysis,* Van Nostrand, New York, 1934.

[10] T. Gray, *J. Soc. Chem. Ind., 32,* 1092 (1913).

sary to delay the analysis, the stopcocks should be sealed with paraffin or sealing wax after the sample has been taken. This should be done by dipping the taps of the gas collector into molten paraffin or wax several times very rapidly so that successive thin layers of wax are formed as a coating. These successive thin layers are a more effective seal than one thick coat.

f. Glass Bottles

Ordinary glass bottles may also be used as gas collectors. However, if vacuum sampling is to be done they must be of strong glass. Bottles used for the bottling of magnesium citrate, the druggists' citrate of magnesia bottles (Fig. 10) are adequate. The rubber washers must be in good condition. One to 2 ml. of mercury may be added at times to act as a seal after the bottle is inverted and prevent the collected gas from coming in contact with the rubber gasket. If the analysis is not to be made shortly after sampling, it is best to seal the top of the bottle in the manner described for sealing the stopcocks of metal gas collectors. If ordinary bottles are used (though they should be used only in an emergency), the cork or rubber stopper should be cut off a little below the neck of the bottle and the recess should then be filled with the molten paraffin or sealing wax.

The procedure to be used in sampling will be described in a subsequent section, for with the exception of some vacuum-type and liquid-displacement gas collectors, it is necessary to use some means to get the gas into the collector.

Traps, bubblers, absorbers, adsorbers, etc., are discussed in Chapter IV.

5. *Aspirating Devices*

In most cases, except where a positive pressure of gas or air is obtainable, it is necessary to use some method or device to pass the air or gas being sampled into the sampling collector or bottle. This is generally done by the principle of aspiration. Aspiration is the action of drawing a gas or a vapor from or through a vessel. An aspirator is an apparatus for drawing a gas or vapor through a tube.

There are two main types of aspirators, the "dry" type and the "wet" type, depending upon whether or not liquid comes directly in contact with the air being sampled. These may be grouped as follows:

Dry Type:
- (1) Aspirator bulb
- (2) Hand and foot pumps

- (3) Water aspirator (so-called filter pump)
- (4) Electric vacuum pump

Wet Type:

- (1) Aspirator bottle
- (2) Liquid displacement gas collectors

a. Dry Type

Aspirator Bulb. Aspirator bulbs are rubber bulbs which have two valves, as shown in Figure 11. When the bulb is squeezed, the air or gas is expelled through valve *a* while valve *b* is closed. On the release of the pressure, valve *a* closes while valve *b* opens, admitting more gas or air.

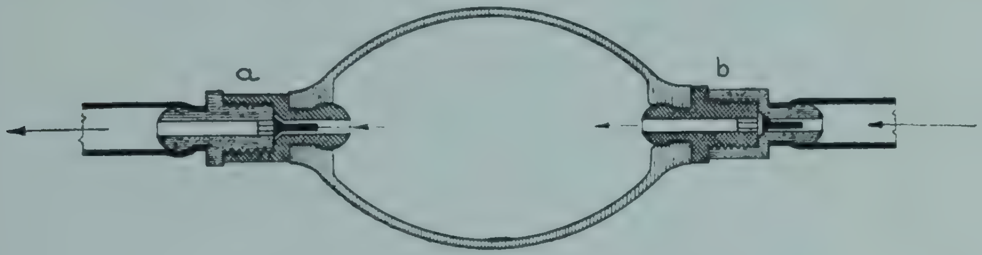

Fig. 11. Rubber-bulb hand aspirator.

These bulbs ordinarily have a capacity of about 40 to 60 ml. In general, it will take about fifty compressions of the rubber aspirator bulb to replace the air in a 250-ml. sample collector.

Aspirator bulbs are simple to use and carry. They can be used almost anywhere. However, the rubber ages so that these bulbs become less efficient with use. The valves leak, at times, because dirt accumulates and lodges in the valve seat. Sometimes this can be remedied by removing the dust and wetting the valve seat. The greatest disadvantage of these bulbs is that the use of them is extremely tedious and fatiguing.

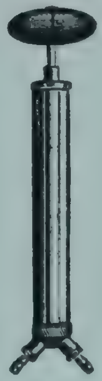

Fig. 12. Hand pump. (*Courtesy Arthur H. Thomas Co.*)

Hand Pump. The British Department of Scientific and Industrial Research has adopted as the official sampling device a hand exhausting pump, somewhat similar to Figure 12, with a barrel of approximately 1.25-inch bore and a capacity of 126 ml. To the inlet end of the pump is screwed a spigot with an external screw $^7/_{16}$ inch, outside diameter 0.437 inch, having 14 threads per inch according to the American National coarse thread dimensions system. To this is screwed a special holder (Fig. 13) containing a test paper, or the sampling train is attached if an absorber is used. On the upward stroke the air to be sampled is drawn through the test paper or test solution and is expelled on the downward stroke by a system of valves analogous to the bulb aspirator. The strokes should be slow and steady and a counter may be attached so that the number of strokes made can be read from the counter.

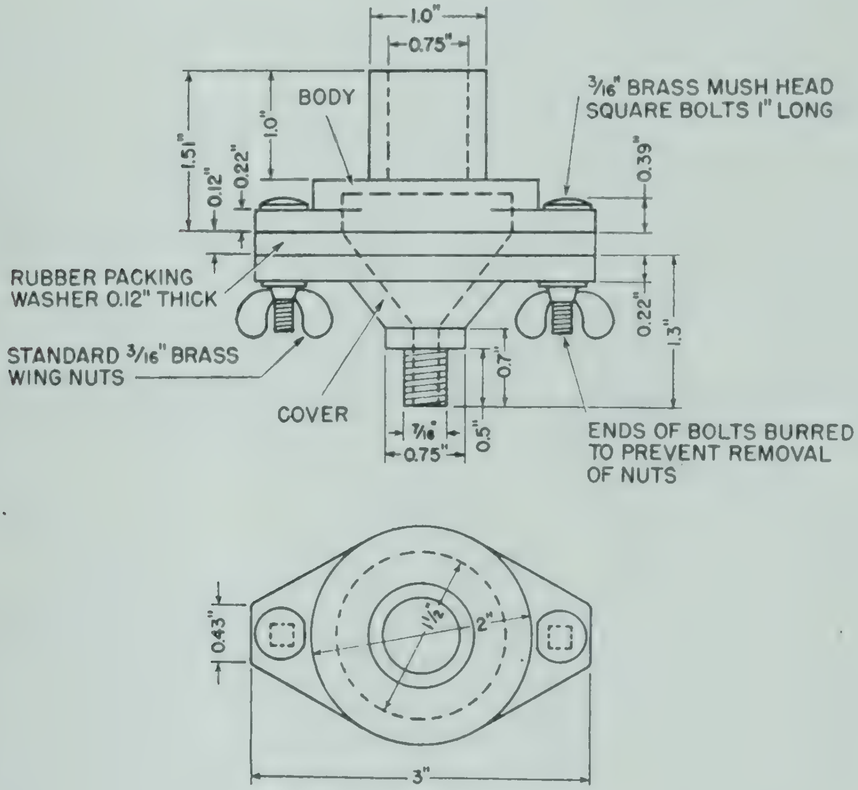
1.0"
0.75"
BODY
3/16" BRASS MUSH HEAD SQUARE BOLTS 1" LONG
1.51"
0.12"
0.22"
1.0"
0.39"
RUBBER PACKING WASHER 0.12" THICK
STANDARD 3/16" BRASS WING NUTS
COVER
7/16"
0.75"
0.5"
0.7"
0.22"
1.3"
ENDS OF BOLTS BURRED TO PREVENT REMOVAL OF NUTS
0.43"
1 1/2"
2"
3"

Fig. 13. Test-paper holder.

Other hand pumps are described by Viles,[11] Haldane,[12] Lee,[13] and Silverman.[14] The pump designed by Lee can also be used as a gas sampler, for when it is clean, dry, and airtight, it will store dry air approximately 24 hours without measurable change in carbon dioxide or oxygen percentage. The Aitken nuclei counter (Chapter V, Section C1) and the

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[11] F. J. Viles, *J. Ind. Hyg. Toxicol.*, *22*, 188 (1940).

[12] J. S. Haldane and J. I. Graham, *Methods of Air Analysis*, Griffin, London, 1935.

[13] R. C. Lee, *Ind. Eng. Chem., Anal. Ed.*, *5*, 354 (1933).

[14] L. Silverman and J. F. Ege, Jr., *J. Ind. Hyg. Toxicol.*, *26*, 316 (1944).

Owens jet dust counter (Chapter V, Section C7b) are also equipped with hand pumps. The pump used for the filter-paper method of Brown is described on page 125.

Midget-Impinger Pump. The midget-impinger pump[15] (Chapter V, Section 7d) is a hand-operated device which has four cylinders set radially at 90° intervals around a single-throw crank. The cylinders and crankcase are formed from an integral aluminum casting. The bore is $1^1/_4$ inches and the stroke is 1 inch, equivalent to a total displacement of 4.9 cubic inches per revolution. The pistons are made of brass and are attached to a mother bearing on the crank. Rotation of the mother bearing about the crank is prevented by attaching one connecting rod rigidly to it. In each cylinder head there is an intake and exhaust valve of the ball-check type with springs. The intake valves connect to a collector ring attached to a check valve in a surge tank. This is connected in turn to the needle valve of a second surge tank. These tanks serve to make the rate of flow uniform by eliminating the variations arising from uneven cranking and from the separate impulses of the four cylinders. With 60 turns per minute of the crank, a flow of 0.1 cubic foot of air through an impinger with a 1-mm. orifice can be obtained. The vacuum at this rate of flow is equivalent to 12 inches of water. Sampling instruments using this pump are commercially available.

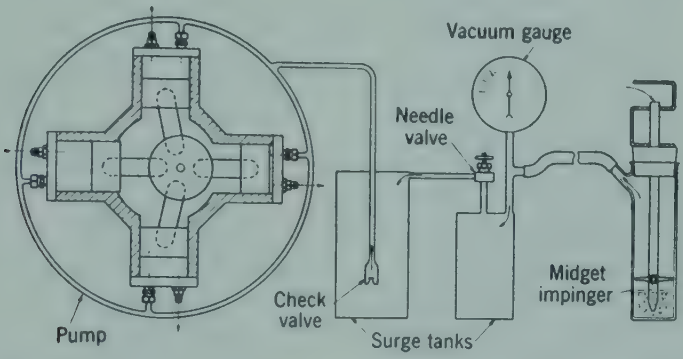

Fig. 14. Pump for midget-impinger sampling apparatus.

Foot Pumps. Where the use of an aspirator bulb or even a hand pump would be extremely laborious, as in the sampling of mine gas, sewer gas, etc., from an inaccessible place, and where there is no water or other type of power easily available, a double-acting foot pump may be used to purge the long sampling extension line. The principle of operation is the same as that of the aspirator bulb, namely, that compression drives the gas out of the pump through one valve and release of the pressure admits the gas through another valve in the pump. These pumps may not be as free from air leakage as desired, especially when sampling by forcing the gas into the collector. In such a case, the foot pump should be used to purge the extension line and the aspirator bulb should be used to fill the gas collector and thus complete the sampling.

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[15] J. B. Littlefield and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3387* (1938).

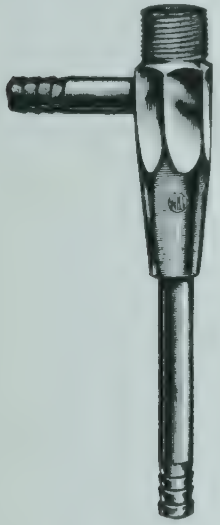
Fig. 15. Filter pump. (*Courtesy Will Corporation*)

Water Aspirator, or Filter Pump. Very likely the simplest device to use for the aspiration of gases is the water aspirator, or common laboratory filter pump (Fig. 15). Almost any one of these devices will be adequate. Where a faucet is available to which an internal or external nipple can be attached, a water aspirator can also be attached. Pressure tubing, wired if necessary, can be used to connect the faucet and pump, where metal nipples are not available or cannot be used. After attaching the water pump, the suction end is attached to the sampling collector and flowmeter, the water is turned on and the sample is taken. Motor driven air pumps, steam injectors and ejectors, water injectors and ejectors, and compressed air ejectors (Fig. 16) operating on a similar principle, may be used if available. A compressed air ejector[16] is described on page 67.

Electric Vacuum Pump. Some electric vacuum pumps are made that can be operated on the power of an automobile battery. There are many portable electric vacuum pumps that can be plugged into a proper electric current line, as, for instance, hand vacuum cleaners. Where the proper electric current as well as the proper electric vacuum pump is available, the sampling procedure can be made easy and rapid.

b. Wet Type

Aspirator Bottles. Where none of the dry-type aspirators is available or for other reasons cannot be used, a simple type of wet-form aspirator can be arranged by the use of two large bottles or small carboys. The bottles should be of at least 5-liter capacity and at least one of the bottles should be calibrated and graduated so that the volume of gas aspirated can be ascertained. Bottle or aspirator A (Fig. 18), which is the one that should be graduated, is filled with water or other suitable liquid such as salt water or water saturated with the gas to be sampled, up to the uppermost graduation. It is connected to the other bottle and to the sampling extension line by means of two glass tubes and a two-hole rubber or other suitable stopper, with one or two screw clamps or stopcocks, as desired. The long glass tube, which should reach the lowest graduation mark, is connected by tubing to the aspirator B. The short glass tube, which should be above the level of the liquid in aspirator A, is connected to the sampling line. By permitting the water or other liquid to flow from A to B, air or gas is drawn into A. The rate of flow, hence the time of sampling, can be regulated by a screw clamp or glass stopcock inserted in the tubing line. The volume drawn in, is known from the calibration of A. The air or gas sampled in this way can be drawn into a gas collector, which is inserted somewhere in the line between the sampling point and the short tube of the aspirator bottle A or through an absorption device as shown in Figure 18, or the aspirator bottle may

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[16] J. Hatch, H. Warren, and P. Drinker, *J. Ind. Hyg.*, *14*, 301 (1932).

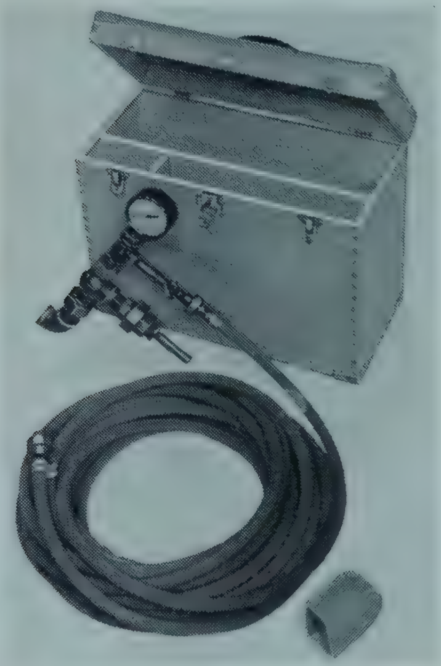

Fig. 16. Air-operated ejector.

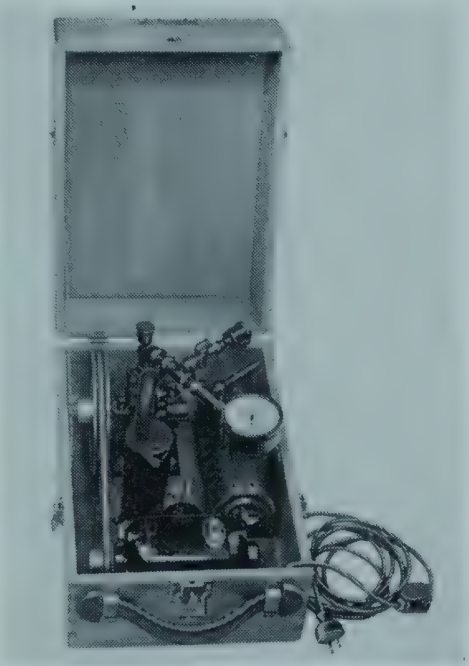

Fig. 17. Motor-driven pump.

(*Courtesy Willson Products, Inc.*)

serve as the gas collector itself. This setup can be simplified by the use of aspirator bottles which have exit openings at the bottom of the bottle. With such devices the liquid need no longer be siphoned over (Fig. 19).

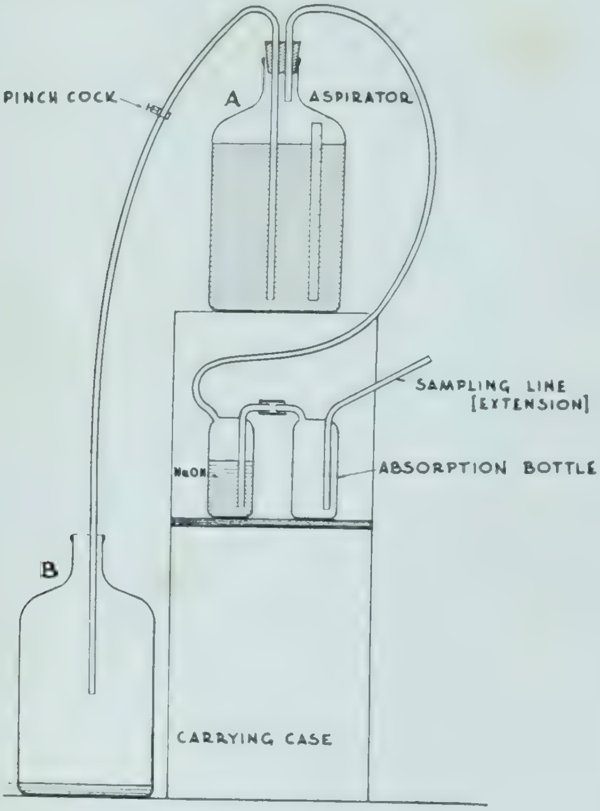
PINCH COCK
A
ASPIRATOR
SAMPLING LINE
[EXTENSION]
NaOH
ABSORPTION BOTTLE
B
CARRYING CASE

Fig. 18. Sampling with aspirator bottles.

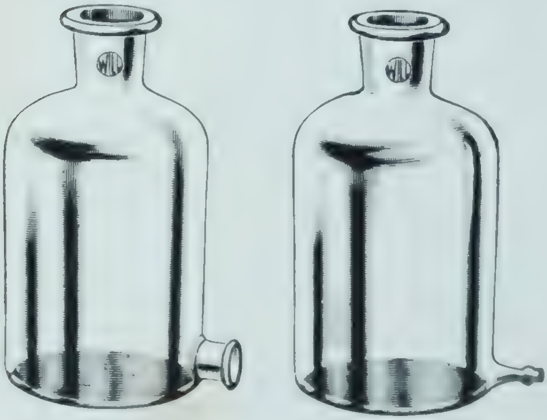

Fig. 19. Aspirator bottles. (*Courtesy Will Corporation*)

Metal aspirators of this form can also be used if they are provided with a glass gauge so that the liquid contents can be ascertained by inspection of the gauge. They are, however, not to be recommended for sampling of corrosive gases or air which contains contaminants that are likely to react with the metal container, unless the absorption apparatus or gas collector is in the line before the aspirator.

Liquid-Displacement Gas Collectors. Actually liquid-displacement gas collectors are also self-aspirating devices, for as the liquid is withdrawn or as it is permitted to flow out, the gas or air to be sampled is drawn into the collector. The use of collectors that have entrance and exit taps is clear. Bottles used as gas collectors must be arranged as is aspirator *A* (in Fig. 18) if they are to act as aspirators. If water is the aspirating liquid, it can generally be discarded. With this type of gas collector or self-aspirator, the rate of sampling can be controlled by the rate of egress of the liquid being displaced.

An aspirating unit made from two 5-gallon gasoline cans is described by Silverman and Wardlow.[17]

6. Sampling Procedure

Before a sample is taken, it is necessary to note the condition of the air or gas being sampled. Thus it must be noted whether the air is moving appreciably, whether the air is stratified and heterogeneous, whether the air is still, that is, air movement less than 25 feet per minute, for a different method of sampling procedure is to be followed in each case. If there is a good air current and there is reason to believe that the air is fairly uniform, and it is desired to take a sample at a given point, only one sample need be taken as representative. If doubt exists, it is best to take more than one sample, following the recommendations given on page 25. If the air is still or is moving only slowly or if there is contamination at a given point, as for instance, where a volatile solvent is evaporating or in a mine where there are gaseous products of explosions, the air in such instances is very likely to be stratified and nonhomogeneous. In this case, it is necessary to take a sample at the given point, which represents the composition only at that point, or to take several samples. In the instance in which several samples are to be taken, the method of dividing a cross section into imaginary rectangles may be used. Take a cross section of a room, mine passage, or other air passage and divide it by eye into equal rectangles. Then take a sample of gas from the center of each rectangle. This procedure is really a modification of the method of sampling by quartering as applied to gases.[18,19]

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[17] L. Silverman and W. B. Wardlow, *Ind. Eng. Chem., Anal. Ed.*, 12, 682 (1940).

It has been made clear from the description of gas-sample collectors and aspirating devices that these devices fall into five sampling groups.

(1) Vacuum displacement
(2) Air displacement
(3) Liquid displacement
(4) Absorption or adsorption in or on some medium
(5) Condensation, freezing, etc.

a. Vacuum Displacement

Where a gas collector having a very high sealed-in vacuum is employed in order to take the sample, it is common procedure to select a straight section of the air course, if there is appreciable air movement of at least 100 feet per minute. If a nick has not been made in the neck of the vacuum tube, make one with a sharp file or other means at an appropriate point to facilitate breaking. Stand facing the air current with the vacuum tube at arm's length. Break the sealed tip by holding the shoulder of the tube in one hand, while the sealed tip is bent and broken by the other hand with some adequate device such as a $^1/_4$- by 3-inch pipe nipple or a small piece of hardwood with a hole slightly larger than the capillary neck, or a pair of pliers, or the head of a cabinet-lock key, or an old-fashioned clock-winding key, or some similar device. The tube should not be struck against a wall or rock, or the roof, ribs, and timbering of a mine, or a bench in a shop: first, if it is broken at any of those points, the sample will be of that point, and second, the tube neck may be broken in such a spot that it will be practically impossible to seal it after the sample has been taken or the tube may be shattered completely and so be entirely useless. When the tip of the tube is broken as has been described, the inward rush of air produces a hissing noise. When the hiss ceases, the tube may be assumed to be full. Hold the tube in place for about 5 seconds after the hissing ceases to be certain sampling is completed. Care must be taken that the break is clean so that no glass particles or obstruction prevents the air from rushing into the tube. If such an obstruction exists, it must be removed.

After sampling has been finished, place the tube in a suitable position

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[18] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products*, Van Nostrand, New York, 1938.

[19] N. H. Furman, *Scott's Technical Methods of Chemical Analysis*, Van Nostrand, New York, 1939.

and seal it with wax[20] by working the metallic cartridge containing the wax over the tip of the collector tube with a twisting motion so that the wax is forced into the capillary opening but not with so much force that it enters into the sample container. Make a tight joint around the shoulder of the tube with the wax which protrudes from the cartridge (Fig. 20). If a piece of wax is used instead of the cartridge, work it around into a ball after forcing it into the capillary tip. The proper type of wax should be prepared at the laboratory by heating two parts of beeswax with one part of Venice, or larch, turpentine. Venice, or larch, turpentine is the type obtained from the European larch. During summer months or for the sampling of gases in warm places, the proportion of beeswax should be increased by 20 per cent. Melt the wax and pour it into empty cartridges—.38 caliber, short, brass cartridge shells—or cut it into pieces of adequate size to give a good ball seal. Do not melt the wax when using it for sealing, for the combustible vapors formed will spoil the subsequent

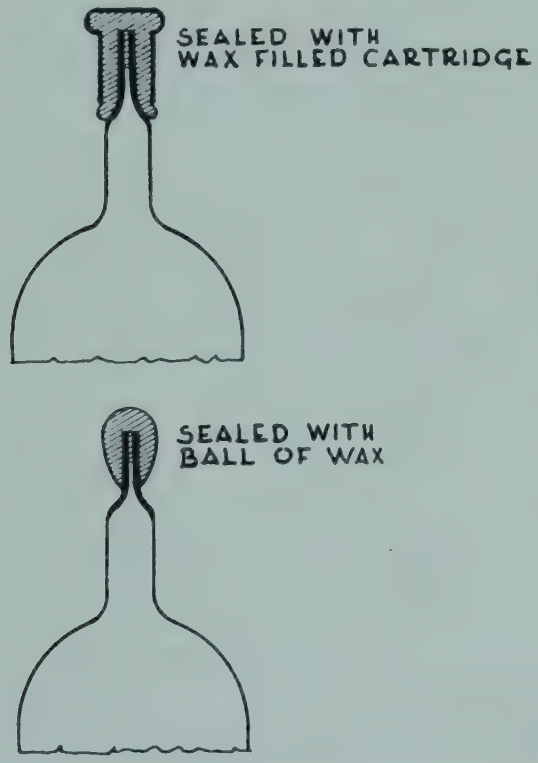

Fig. 20. Sealing vacuum-tube collectors.

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[20] G. A. Burrell, F. M. Seibert, and G. W. Jones, *U. S. Bur. Mines, Bull. 197* (1926).

analysis. Do not use chewing gum, paraffin wax or tar, as these substances do not form a proper seal with the glass.

When the vacuum tube is used to sample a gas or air in an inaccessible place, such as the blister or hold of a ship, a tank car, behind a fire or gas seal in a mine, or a sewer or manhole, the following procedure may be used. An extension line or tube, preferably of glass or metal that will not be attacked by or react with the components of the gas or air being sampled, to which is attached an end of rubber tubing or an adequate coupling device, is placed, pushed, or dropped, as the case may be, to the point to be sampled. When sampling at the point at which a workman breathes, the extension line must be fixed at that point by some device. If the workman moves in a limited area, arrangement must be made to have the connecting line move with him. The length and volume of the extension line should be known. It should then be purged with one of the aspirator devices previously described. At least 10 to 15 times the volume of the gas to be sampled should be used in the purging process. After purging, close the rubber end of the tube with a pinch clamp or with some stopcock arrangement or use the T-tube method illustrated in Fig. 25. As quickly as possible fit the line tightly over the neck of the vacuum tube. Break the tip by grasping and bending as shown in Fig. 21. Wait $^1/_2$ minute for the tube to fill. Remove from the extension line and seal as described previously.

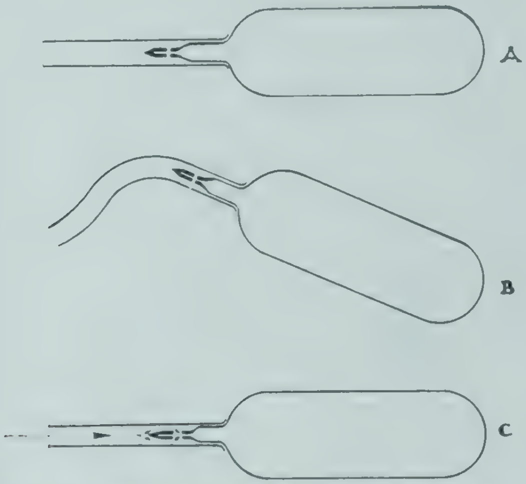

Fig. 21. Method for filling vacuum containers through extension hose leading to inaccessible places.
A. After purging hose, tightly insert shoulder of container.
B. Break tip by grasping tip in one hand, the container in the other, and bend hose.
C. Allow gas to flow past loosely fitting end of broken tip into container.

An alternative device has been described by Fene.[21] It employs a common snap-type mousetrap to break the neck of a vacuum tube at the place where it is desired to collect the sample. A mousetrap is mounted on one end of a block of wood $11^3/_4$ by 3 by $^3/_4$ inches in such manner that a lead weight attached to the trigger will spring the trap when the device is given a sharp jerk. A vacuum tube is placed on the other end of the block and held in place by a strong rubber band. A strip of corrugated rubber is placed on each side of the grooved block to prevent the tube from slipping when the sample is taken. An adjustable shoulder, provided with a rubber cap, is placed so that the neck of the vacuum tube will rest on it. The shoulder is made adjustable to accommodate various sizes of tubes and to keep the neck of the tube from breaking too far back from the point. A metal handle is fastened to one end of the block, with a hole in the end through which the brass wire used for lowering the device is tied. The device is enclosed by a strong wire-gauze covering, hinged on one side and so arranged that it can be locked shut on the other side. This covering prevents breaking of the tube while it is being lowered or raised in a shaft or other place. Brass wire of not less than 22 gauge should be used for lowering the device. A drawing of the device is shown in Figure 21A.

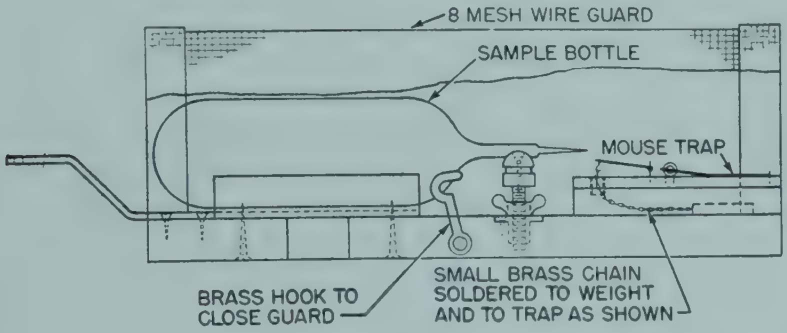
8 MESH WIRE GUARD
SAMPLE BOTTLE
MOUSE TRAP
BRASS HOOK TO CLOSE GUARD
SMALL BRASS CHAIN SOLDERED TO WEIGHT AND TO TRAP AS SHOWN

Fig. 21A. Sampling device for collecting gas samples in inaccessible places.[21]

In collecting air samples in shafts, sewers, gas wells, or empty oil tanks, a vacuum tube is adjusted so that the spring of the trap will hit the neck of the tube about halfway between the file mark and the tip of the tube. The trap is set, making certain that the lead weight is extended downward as far as possible. The device is lowered in a vertical position to the point where the sample is to be collected, and the lowering wire is given a sharp jerk, which will cause the trap to spring and break the neck of the tube. The device is pulled quickly to the surface and a seal placed on the opening in the neck of the tube. Under ordinary atmospheric pressure, none of the sample will be displaced in the tube while it is being raised to the surface. Samples have been collected with this device in shafts at depths of 450 feet and through a 6-inch vent pipe in a concrete seal over an air shaft. The device permits collection of samples at any desired place in a shaft or well.

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[21] W. J. Fene, *U. S. Bur. Mines, Inform. Circ. 7122* (1940).

In collecting samples from behind seals in mines it is necessary to provide the seal with a pipe large enough to permit passage of the sampling device. With the cover removed, the device can be passed through a 3-inch pipe. To collect a sample of air from behind a seal, the device should be fastened securely to a pole or rod and pushed through the pipe, making sure that the lead weight connected to the trigger of the trap is extended as far as it will go. A sharp jerk forward will cause the trap to spring and break the neck of the tube.

Continuous Sampling Device. When gas flows through a fixed orifice inserted in a tube, its velocity increases with the pressure drop across the orifice until the ratio of upstream to downstream pressure is about 2:1. When this ratio is reached the gas passes through the orifice at the velocity of sound, and further increase in pressure drop has no effect on gas velocity, which is now independent of both upstream and downstream pressures.[22] The ambient volume flow rate is also constant and the mass flow rate is proportional to the upstream density.

If a flask is evacuated and ambient gas is permitted to enter through a small orifice inserted in an inlet tube, the ambient volume flow rate remains fixed, regardless of ambient pressure, until the internal pressure reaches half ambient. If the flow is allowed to continue beyond this point, it falls off gradually until pressure equilibrium is reached. By proper choice of flask volume and orifice area, the period of constant flow may be varied within wide limits. If two stopcocks and a pressure gauge are fitted to the flask, the result is an acoustic flow device that can be used to sample ambient air at a constant rate over any desired period of time.

The apparatus is detailed in Figure 21B. The collecting flask must be able to withstand a vacuum and have a convenient size and weight. U. S. Army-type low-pressure aviation oxygen cylinders were found satisfactory. Orifices of 50 to 165 μ in diameter permit flows of 25 to 250 ml. per minute. These are most convenient in practice. Such orifices can be made easily by drilling disks of metal foil or by piercing such disks with a sharp needle. The disks may be cemented between washers and mounted as indicated in Figure 21B. The flows indicated are small and it is therefore important to use care in sealing all joints to avoid residual leakage. The internal pressure is best measured with an accurate absolute pressure gauge. A differential-pressure or vacuum gauge will also serve, but it is then necessary to determine the ambient pressure for each reading. A filter is desirable where dust or smoke particles may clog the orifice; however, it should introduce only a very small pressure drop. The dead space between the intake nozzle and the control stopcock should be small enough to introduce very little time lag in the gas collection. The inlet tube may be rubber pressure tubing, $^1/_8$ to $^1/_4$ inch diameter and 5 to 10 feet long, which will generally be long enough to permit the flask to be put in a convenient place.

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[22] D. E. Goldman and J. A. Mathis, *Naval Med. Research Inst.*, ***Research Project*** X-417, *Rept. 4* (1945).

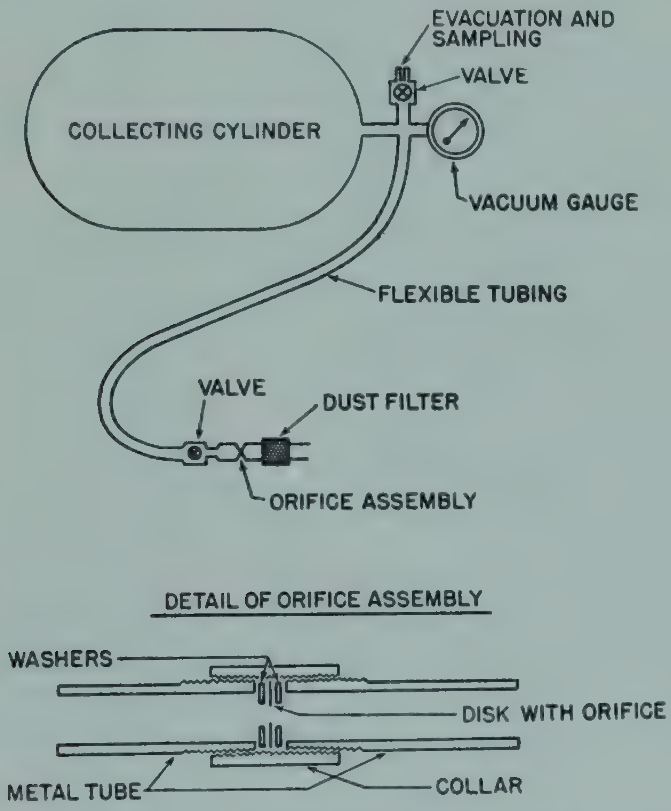
EVACUATION AND SAMPLING
VALVE
COLLECTING CYLINDER
VACUUM GAUGE
FLEXIBLE TUBING
VALVE
DUST FILTER
ORIFICE ASSEMBLY
DETAIL OF ORIFICE ASSEMBLY
WASHERS
DISK WITH ORIFICE
METAL TUBE
COLLAR

Fig. 21B. Diagram of fixed-orifice-type continuous gas-sampling device.[22]

Sampling Procedure. Before use, the apparatus must be evacuated to a pressure low enough to keep the constant-flow period within proper limits. Under ordinary conditions a water-sealed pump or an aspirator is satisfactory; however, a high-vacuum pump can be used also. After the apparatus has been evacuated, the valves are closed and the flask is set up for the test with the intake nozzle placed so as to sample at a desired point. As the orifice valve is opened, the internal pressure and time are recorded. At the end of the collection period, as the valve is closed, the internal pressure and time are recorded again, and the device is ready to have a sample taken for analysis. Since the flask is still half evacuated, it is good practice to fill it with clean air up to ambient pressure, particularly when time will elapse before an analysis is made. This procedure minimizes the effect of residual leaks but a correction factor must be applied to the analytical results.

Analytical Procedure. Connect a clean gas sampling tube to a leveling bulb with about 2 feet of rubber tubing and fill the system with water. Connect the inlet of the gas sampling tube to the outlet nipple of the collecting flask with a short piece of rubber tubing fitting the glass as near to the metal as possible. With the stopcocks open, lower the leveling bulb until about 30 ml. of water is displaced by gas from the flask. By proper manipulation of the stopcocks, close off the flask and open the sampling tube to the outside. Raise the leveling bulb to displace the gas from the sampling tube with water. This process serves to flush out dead-space air and should be repeated one or twice. Finally, take the gas into the sampling tube, fill it completely, and retain it for analysis.

The use of a water-sealed collecting system requires that the gas in the collecting flask be diluted to ambient pressure with clean air, that is, air free from carbon monoxide, mercury, organic solvents, etc. The volume of the sampling tube must be large enough to hold the amount of gas required for analysis, but should be small compared to the volume of the collecting flask. For example, with a 16-liter collecting flask and a 200-ml. sampling tube, two partial flush-outs and one filling of the sampling tube remove less than 300 ml. from the flask, which is 2 per cent of its volume. Thus a suction of 15 mm. of mercury, or about 7 inches of water, is required. The entire sampling process may be performed, if necessary, three times with the 2-foot tube from the sampling tube to the collecting flask. Analyses for specific compounds may be performed as described in the text.

Calculations. The time average partial pressure p of the gas under study may be calculated from the concentration C, in the flask, using the formula

$$\bar{p} = \frac{V}{ut} p_3 C$$

where: V = volume of the flask, including the inlet tube and pressure gauge
u = ambient volume flow rate
p_3 = pressure in the flask
t = duration of the collection period

If the sample is diluted to atmospheric pressure, p_3 is simply the barometer reading. This formula is strictly valid only when the ambient temperature is constant throughout the test run. The error introduced by a temperature variation of 60° C., in 1 hour, is only 5 per cent, hence in practice this formula may be used for a wide variety of field conditions.

Vacuum Bottle. The method of sampling with vacuum bottles evacuated at or near the point of sampling has been described in connection with the description of the bottle itself (Section 4b). Inaccessible places may be sampled, as explained in the previous paragraph, with the use of an extension line connected to the arm having stopcock *a* in Figure 5. The volume sampled must be computed, for the residual pressure is generally sufficiently great to introduce a volume error if not corrected by calculation.

Illustrative of the use of evacuated bottles in sampling at a distance, is the electrical method for sampling for hydrocyanic acid used as a fumigant in ships.[23]

> A Winchester quart bottle closed with a rubber stopper is evacuated through a capillary tube, which is then sealed hermetically. It is placed horizontally in a wicker frame and a weight is attached to the end of the capillary tube by a cord about 2 feet in length, and also by a short piece of fusible wire as shown in Fig. 22. The electric wires are connected with the two ends of the fuse wire so as to form a closed circuit which can be operated from a distance. On passing a current sufficiently strong to fuse the wire, the weight is released, which on falling to the full length of the cord causes the fracture of the capillary, and thus permits the surrounding air to enter into the bottle. The vacuum sampling containers can be set before the fumigation begins. Sampling can then take place when desired and the samples collected after the hold is clear of gas.

A simpler method that does not require the use of electricity, which is not always available, is the following.[23]

> A Winchester quart bottle, fitted with a ground glass stopper with a sealed-in capillary tube reaching almost to the bottom of the bottle, is evacuated through its side arm and sealed hermetically as shown in Fig. 23. The part of the capillary above the side arm ends in a stout glass ring to which may be attached a thin cord

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[23] P. G. Stock and G. W. Monier-Williams, *Repts. Pub. Health Med. Subjects, 19*, Ministry of Health, London, 1923.

or wire. At point *A* the capillary tube in nicked with a file so that on pulling the cord the capillary will break readily at that point. The evacuated bottles are placed in position before fumigation and are tied to stanchions or other supports. Cords or wires are attached to the rings and are led out to the deck or dock side through keyholes, hatch covers, small openings, etc., so as to give a direct right-angle pull on the capillary tube. The samples may than be collected after the hold, compartment, or room is free of gas.

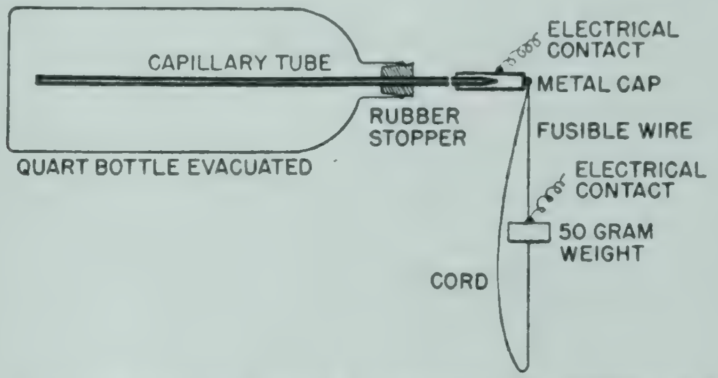
ELECTRICAL CONTACT
CAPILLARY TUBE
METAL CAP
RUBBER STOPPER
FUSIBLE WIRE
QUART BOTTLE EVACUATED
ELECTRICAL CONTACT
50 GRAM WEIGHT
CORD

Fig. 22. Vacuum sampling bottle for sampling in inaccessible places.

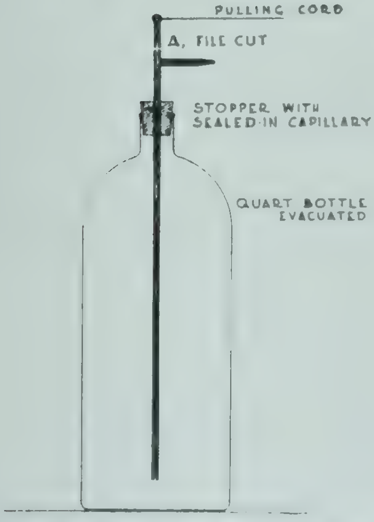
PULLING CORD
A, FILE CUT
STOPPER WITH SEALED-IN CAPILLARY
QUART BOTTLE EVACUATED

Fig. 23. Vacuum sampling bottle for sampling in inaccessible places.

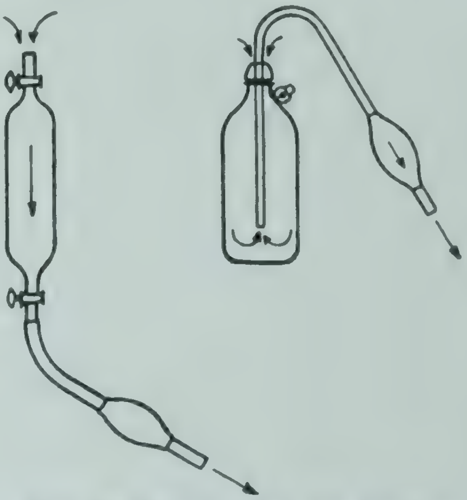

Fig. 24. Sampling by gas displacement. The atmosphere sampled should be discharged outside sampling zone.[24]

In both instances, a reagent with which the contaminant will react may be placed in the vacuum bottle before evacuation. In the case of hydrocyanic acid, 50 ml. of 0.04 *N* sodium hydroxide solution is used.

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[24] W. P. Yant and L. B. Berger, *U. S. Bur. Mines, Miners' Circ.*, 34 (1936).

b. Air Displacement

Where sampling by air displacement is desired, the methods illustrated in Fig. 24 may be used. The rubber aspirator symbolizes the position of the aspirating devices that may be used. It is necessary to purge the entire line and the gas collector itself with at least 10 times the capacity of both the gas collector and extension line, when they are used to get at an inaccessible place. Thus, for example, it will require 50 squeezes of the ordinary 50-ml. rubber bulb aspirator to take a 250-ml. sample. The tube or bottle should be held in place after the required amount of purging and sampling has been completed until the gas collector has been sealed and the aspirating device removed. Where sampling by gas displacement from inaccessible places is necessary, the position of the gas collector, aspirator, and extension line should be as is indicated in Figure 25. Purging and sampling then proceed as described.

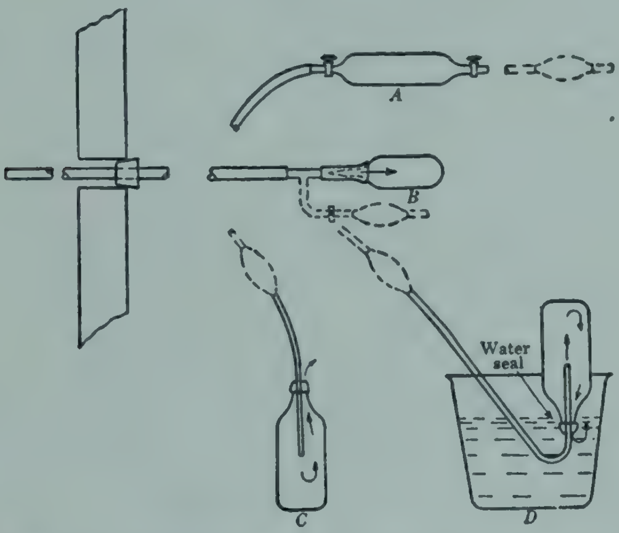

Fig. 25. Sampling by gas displacement from inaccessible places.[24]

c. Liquid Displacement

As was explained in the section on aspirators, liquid displacement gas collectors are actually self-aspirators. The procedure of sampling where the place of sampling is accessible is very simple and convenient. The liquid in the gas collector is run out by draining or pouring within the zone of the gas to be sampled and then the container is closed and sealed. The liquid to be used depends on the type of sample. Water, water saturated with the gas or gases to be tested, salt solutions, and mercury are the ordinary liquids used. Solutions of gas and salts, and mercury are used to minimize and eliminate solubility errors. Where the solubility of a gas is very small, this precaution is unnecessary. Where mercury is used, it should, of course, be poured into another container and not be permitted to escape on the ground or floor.

Sampling by liquid displacement from places not within easy reach, and which therefore require an extension sampling line, is performed in an entirely analogous manner to the procedure previously described. The extension line must first be purged of the ordinary air it contains with 10 times its volume of the air to be sampled by means of some independent aspirating device. Then the extension sampling line is attached to the liquid displacement gas collector and the liquid is permitted to drain or pour out as illustrated in Figure 26. Capillary extension tubes may be attached to the exit tube of the gas collector to prevent back flow of air, or tubes with an internal extension tube may be used for the same purpose. Gas collector tubes with 3-way stopcocks and extra tubulatures at the entrance tap simplify the purging procedure, for the use of T tubes is no longer necessary. The extension line may be purged through the side tubulature. The rate of sampling when using liquid-displacement gas collectors is controlled by the rate of exit flow of draining or pouring.

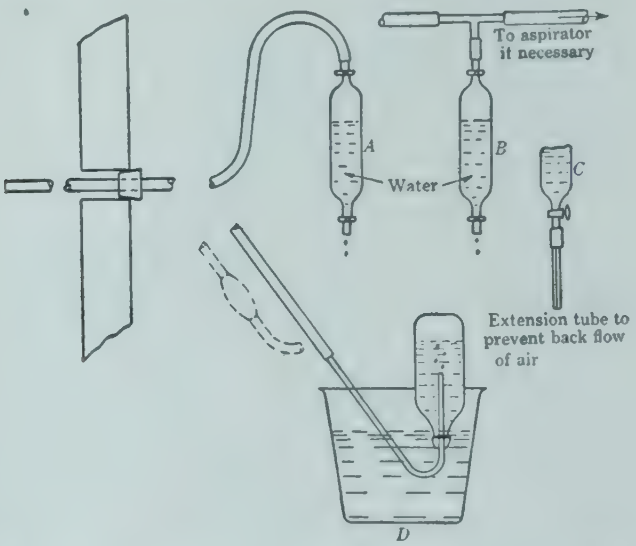

Fig. 26. Sampling by water displacement from inaccessible places.[24]

d. Absorption and Adsorption

The most useful method of sampling where large volumes of gas have to be handled in order to obtain the necessary amount for adequate analysis of a component present in minute quantity is that of absorption or adsorption of the component to be estimated by some agent. Some absorbers, traps, bubblers, absorbents and adsorbents will be discussed in Chapter IV. An absorber containing the absorbing medium is placed in the sampling line after that line has been purged with the air to be sampled. Then a sufficient quantity of the air being sampled is aspirated at a rate sufficiently rapid to pass through enough air to give an adequate estimation, but this flow must not be so rapid that the ingredient to be determined fails to be absorbed. A flowmeter of some type or other gas measurement device must also be in the line so that the amount of gas sampled will be known. If necessary, other absorbers must be in the line. Thus, after using a very strong acid absorbing medium, it is necessary to place an absorber containing sodium hydroxide or other alkali to neutralize any acid that may be carried over during the aspiration process. (See Fig. 18.)

In general, where homogeneous solutions are obtained by use of an absorber as a result of the reaction or solution of the component being estimated with or in the absorbent, rinsings should not be combined with the sampling fluid. The volume of the absorbent recovered should be noted. This practice avoids unnecessary dilution of the sample.

e. Other Sampling Procedures

If a gas under positive pressure is to be sampled, as is the case with gas cylinders or in a main provided with outlet cocks, the gas collector must be attached by some short extension line to the cylinder or to the outlet taps of the main. After purging the sampling line with the gas to be examined by permitting 4 or 5 volumes of that gas to pass through the connecting tube and some side arm or through the collector itself, if the gas displacement method is being used, the gas collector is permitted to be filled under the outward pressure of the gas itself, and the cocks are closed and then sealed.

Syringes such as Luer syringes have been used for sampling, principally for field determinations. Illustrative of such procedures are those of Patty and Petty, and Jacobs and Brody for nitrogen dioxide–nitrogen tetroxide mixtures detailed in Chapter IX, for the determination of

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oxygen,[25] and for the estimation of carbon monoxide.[26,27]

Brief mention should be made of the sampling of hot gases, occluded gases, and gases under reduced pressure. Where hot gases have to be sampled, glass, heat resistant glass, quartz, porcelain, and metal connecting tubes must be employed according to the temperature of the gas. Porcelain tubes should be preheated and metal tubes should be cooled by a condenser jacket.

Where occluded gases or gases under reduced pressure are desired for analysis, they must be swept out into the sampling vessel by some means or must be pumped out by the use of a Toepler pump[28] or its equivalent, or they must be obtained by aspiration.

If a gas is to be sampled in a flue or large pipe where the composition varies considerably between the sides and center of the flue, an extension tube, passing through the pipe from one side to the other cross-sectionally, having openings at different points along its length or a length-long slit, comparable to the slot in a sampling tube, may be used to obtain a sample or a number of samples can be taken at different points.

It is well to remember that very likely the safest procedure from the point of view of accuracy is to take duplicate samples for any point sample, if at all possible.

f. Sampling Data

In order that one may correlate the analysis of a sample of air or gas with the sampling, certain pertinent data must be known. These data may be listed as follows:

(1) Identification Purposes
  (a) Sample number
  (b) Sample type
  (c) Date, time, place, and locality
  (d) Name of inspector or collector
  (e) Method of sampling

(2) Computation Purposes
  (a) Pressure
    Barometer reading and all other pressures needed, such as residual and final pressures in vacuum bottle sampling, or outward or negative pressure in a mine fire seal

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[25] Y. Henderson and L. A. Greenberg, *J. Am. Med. Assoc.*, *96*, 1474 (1931).

[26] A. N. Setterlind, *Ind. Hyg. Newsletter*, *8*, No. 2, 7 (1948).

[27] A. N. Setterlind, *Ind. Hyg. Quarterly*, *9*, 35 (1948).

[28] G. Lunge and H. R. Ambler, *Technical Gas Analysis*, Van Nostrand, New York, 1934.

(b) Temperature
    Wet bulb } if necessary
    Dry bulb }
(c) Humidity
(d) Velocity
(e) Quantity

With the data of group (2), the gas calculations given in the section on the measurement of quantity in gases, Chapter III, Section B, may be performed.

Selected References

Burrell, G. A., F. M. Seibert, and G. W. Jones, "Sampling and Examination of Mine Gases and Natural Gas," *U. S. Bur. Mines, Bull. 197* (1926).

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Jacobs, Morris B., *Chemical Analysis of Foods and Food Products,* Van Nostrand, New York, 1938.

Lunge, G., and H. R. Ambler, *Technical Gas Analysis,* Van Nostrand, 1934.

Owings C. W., "Sampling Dust in Rock-Dusted Mines," *U. S. Bur. Mines, Inform. Circ. 6129* (1929).

Yant, W. P., and L. B. Berger, "Sampling Mine Gases," *U. S. Bur. Mines, Miners' Circ. 34* (1936).

CHAPTER III

Measurement of Gas Volume and Quantity

When large volumes of gas are to be analyzed for particular contaminants, they are generally passed through some absorbing medium or agent. In order to correlate the analysis with the volume of gas sampled, that volume must be known and hence must be measured. Not only does the volume of gas used for the analysis need to be known, but often the industrial-hygiene chemist must know the velocity of elimination of gases by means of ducts, vents, and the like. He is also interested in the velocity of air in the workroom, itself, as a measure of ventilation. Therefore both instruments used merely for air velocity as well as for estimation of gas volume will be described.

The various measuring devices used fall into two main divisions. In the first group are those instruments which measure all the gas that passes and in the second group are those devices which measure the velocity of flow. Knowing the characteristics of the instruments of the second, the time of flow, and the velocity, the amount of gas passed can be calculated by formulas. Some of these velocity instruments are equipped with volume charts; others are graduated to read volume of gas flow directly.

A. CLASSIFICATION OF GAS MEASUREMENT DEVICES

1. Total gas volume instruments
    - Wet meter
    - Dry meter

2. Gas velocity instruments
    - Anemometer
    - Pitot tube
    - Venturi meter
    - Orifice meter
    - Gas flowmeter
    - Constant flowmeter
    - Capometer
    - Rotameter
    - Thomas electric gas meter
    - Thermo-anemometer
    - Kata thermometer

1. Total Gas Volume Instruments

Wet Meter. The wet meter (Fig. 27) is the principal instrument for measuring total gas volume. It is an apparatus generally made of brass tinned to withstand corrosion. It consists of a cylindrical case which contains a rotor drum suspended in a liquid, on a horizontal axis. This drum is divided by metal vanes into four spiral compartments of exactly equal volume. The gas is led in from a cock through an opening near the axis in each chamber and emerges from an opening near the periphery of the drum. The liquid used is water or glycerol, the height of which is measured by means of a glass gauge attached to the case. The liquid is usually set at half height but may be adjusted, if desired, to some other height. The pressure of the incoming gas causes the drum to rotate. An indicator

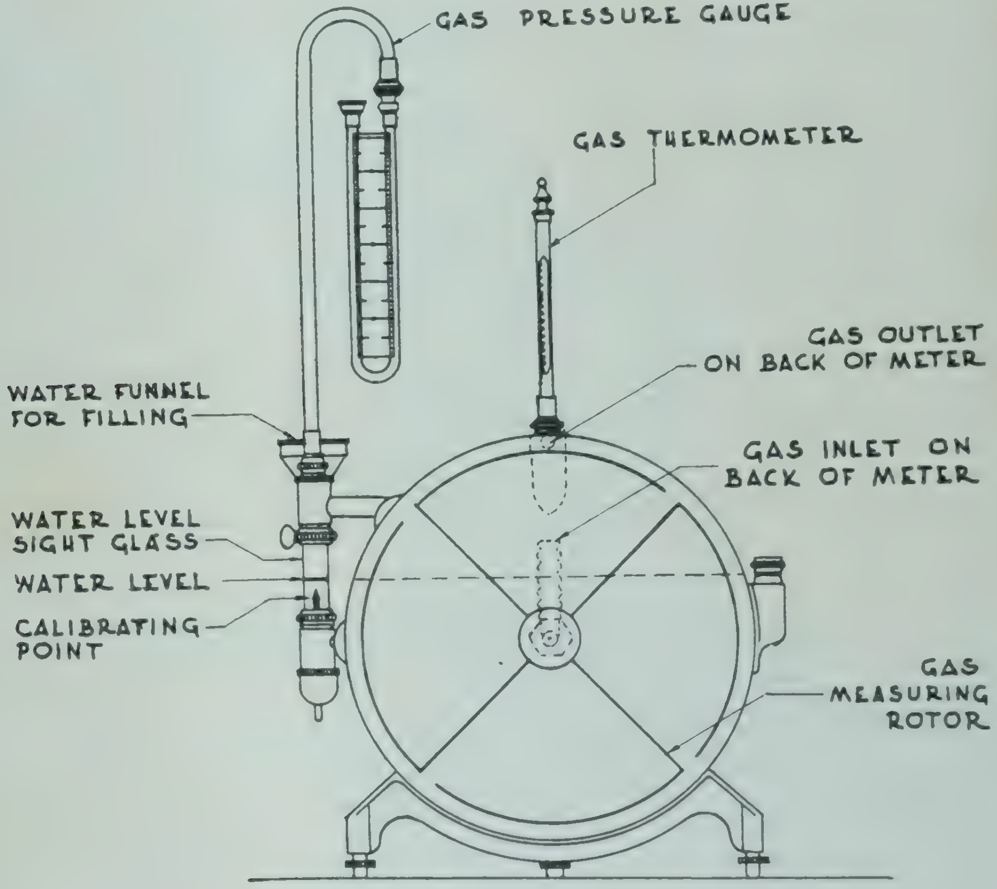
GAS PRESSURE GAUGE
GAS THERMOMETER
GAS OUTLET ON BACK OF METER
WATER FUNNEL FOR FILLING
GAS INLET ON BACK OF METER
WATER LEVEL SIGHT GLASS
WATER LEVEL
CALIBRATING POINT
GAS MEASURING ROTOR

Fig. 27. Wet gas meter. (*Courtesy Emil Greiner Co.*)

hand is attached to the drum, which registers the volume passed on a dial as the drum rotates. Some instruments are constructed so that the indicator makes a complete revolution for $^1/_{10}$ cubic foot. Wet meters must be equipped with spirit levels and leveling screws so that the case may be set evenly to allow the drum to rotate freely. They must also be fitted with a thermometer and pressure manometer so that the measured gas volume may be reduced to standard temperature and pressure if necessary. A modification of this type of instrument is one in which the rotor drum is suspended inside of a case, the upper part of which is made of glass, so that the rotating drum is visible.

Dry Meters. Dry meters are meters of the positive displacement type. The entering gas or air stream moves diaphragms or bellows. The movement of the diaphragms operates a crank that transfers the motion to a rotating indicating hand on a scale. These instruments are used mainly for measuring rapid and large volumes of gas. They are also used to calibrate flowmeters. They are not often used in industrial-hygiene analysis.

Neither the wet type nor the dry type of meter can be used with corrosive or acid gases. For such gases a simple meter made of glass containing a liquid, which siphons over each time the apparatus is filled to a definite volume may be used.[1]

2. Gas Velocity Measurement Instruments

The flow of a fluid, especially of a gas, is difficult to measure. The distinction between a flowmeter and a quantity meter, such as a wet or dry meter, is that flow is a quantity passing a given section of a conduit per unit of time and is expressed as liters of gas per minute, for example 7.0 liters per minute; or as cubic feet of gas per minute, gallons of water per minute, pounds of steam per minute, etc. The more important instruments for the measurement of gas flow used in the chemistry of industrial hygiene are the devices adapted for the measurement of gas velocity. Some of the more generally used are the Pitot tube, the Venturi meter, the orifice meter, and the common gas flowmeter. These instruments and others that are used will be described.

Anemometer.[2] One of the simplest of the velocity type instruments to use is the anemometer (Fig. 28). These instruments are somewhat expensive, if carefully made, and require frequent adjustment. The anemometer is held in the air stream so that the air flow rotates its blades or the gas is directed so that it hits and rotates the blades of the instrument. The rotation of the vane is registered on a calibrated tachometer. The instrument must be used with a stop watch, for the dial reading gives the result in linear feet of air travel.

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[1] E. G. Beckett, *J. Soc. Chem. Ind.*, *36*, 52 (1917).

[2] E. Ower, *Measurement of Air Flow*, Chapman ɴ Hall, London, 1933.

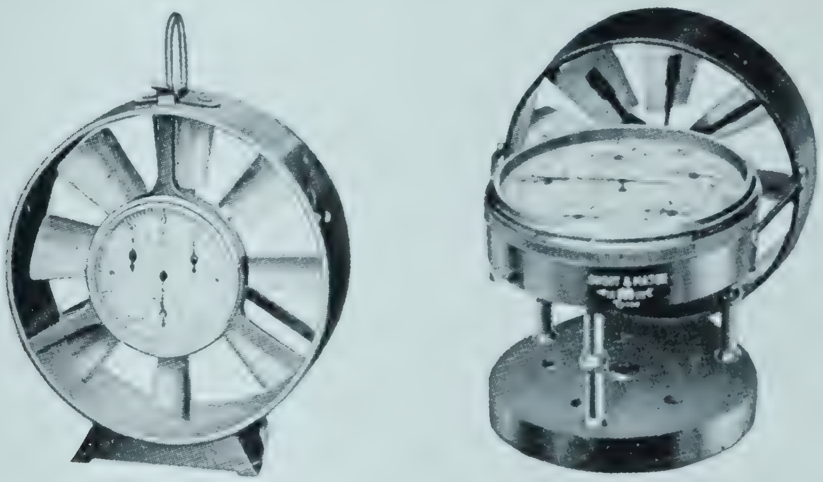

Fig. 28. Anemometers. (*Courtesy Chicago Apparatus Co.*)

A common type of anemometer[3] consists of a metal cylindrical frame about 3 or 4 inches in diameter and 1.5 or 1.75 inches wide, with a base or legs on the bottom so that the instrument will not roll when set down. Sometimes the device is equipped with a small metal loop which serves as a hand hold. Attached to a light axle that has a relatively frictionless bearing are a number of arms to which are attached blades. The blades, arms, and axle are known as the vane, one revolution of which corresponds to an air velocity of 1 foot per minute. Either at the center of the device attached to its frame by arms or supported on separate legs is the calibrated tachometer, consisting of a number of dials with pointers. On the large dial comprising the face is a circle with 100 divisions, each division representing one revolution of the vane. Thus one complete revolution of the pointer is equivalent to 100 feet. Within the large dial are a number of smaller ones that indicate hundreds, thousands, ten thousands of feet, respectively, depending on the number of dials. A catch or lever is provided which permits the vane to be engaged or disengaged at will. Some devices are equipped with a lever that resets all the dials to zero.

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[3] G. W. Grove, *U. S. Bur. Mines, Inform. Circ. 7037* (1938).

To use the anemometer it should be placed or held so that air will flow through the anemometer from the back or sides opposite the dials. As Grove points out, the anemometer, when used in a mine, should be held at arm's length, as nearly perpendicular as possible to the air current. It should be moved regularly and slowly, up, down, and across the airway, so as to obtain an average reading of the air velocity. This is necessary because the velocity of air in a mine is generally greater at the center of a passage than near the bottom, sides, or top. If it is desirable to obtain readings that can be compared, it is preferable to post the anemometer in the same spot, at stated periods.

To take a reading, place the anemometer as described, push the lever to the on position and note the exact time. At the end of a known time interval, say one or more minutes, push the lever to the off position, stopping the dial pointers, and read the velocity. This will be in linear feet per minute. To obtain the amount of air passing the reading position, it is necessary to make a calculation by multiplying the linear velocity by the area at the point at which the reading was made. Thus if the areaway is 12 feet wide and 7 feet high, corresponding to a cross section of 84 square feet and the linear velocity is 200 feet per minute, there will be a flow of 16,800 cubic feet per minute. Average anemometer readings will give average flow rates.

These devices will not function well if the velocity of the air is under 30 feet per minute. Readings will not be accurate if the velocity is under 80 to 100 feet per minute.

Velometer. The velometer[4] is an instantaneous direct-reading air-velocity instrument that can obtain spot velocities over a very small area in ranges from 20 feet per minute to 2,500 feet per minute and 3 inches static or total pressure. Special arrangements of this instrument can measure up to 25,000 feet per minute and 20 inches pressure.

The impact or pressure of the air entering the meter, with or without the aid of jets of different types and shapes, actuates a vane mounted on a jeweled movement. A pointer is attached to the vane.

This meter indicates air velocities directly on a scale in feet per minute without the necessity of timing or the use of mathematical calculations. It can be used for measurement of air flow in ducts, grilles, flues, etc., and to locate leaks and drafts.

Since this is a velocity instrument, the volume of air flow must be computed. The total cubic feet of air per minute (c. f. m.) is equal to

[4] Alnor Velometer, Illinois Testing Laboratories, Inc., Chicago, Ill.

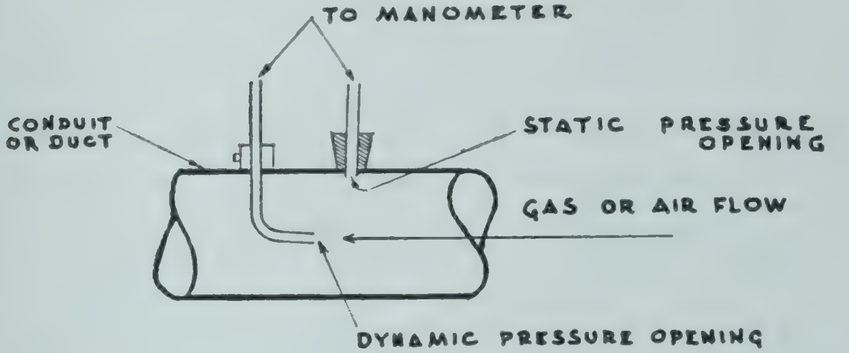
TO MANOMETER
CONDUIT OR DUCT
STATIC PRESSURE OPENING
GAS OR AIR FLOW
DYNAMIC PRESSURE OPENING

Fig. 29. Simple Pitot tube.

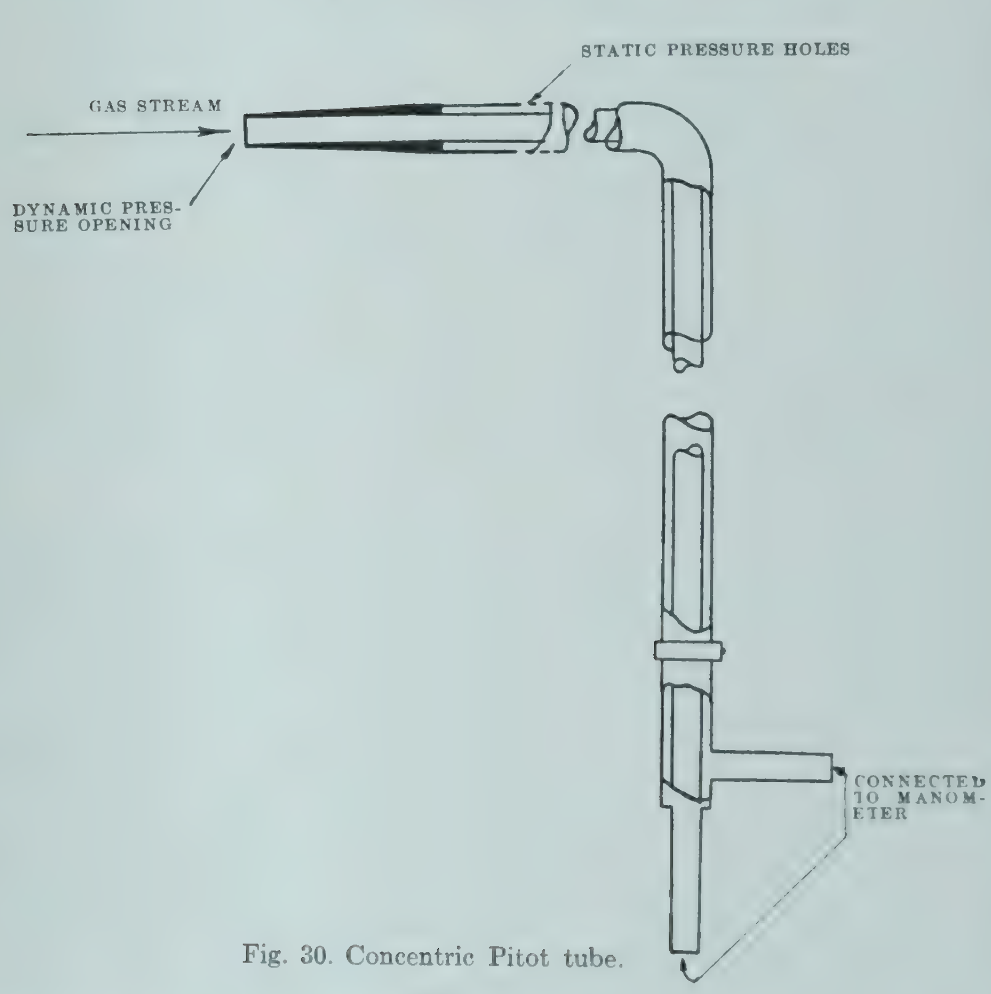
STATIC PRESSURE HOLES
GAS STREAM
DYNAMIC PRESSURE OPENING
CONNECTED TO MANOMETER

Fig. 30. Concentric Pitot tube.

the product of the average velocity reading in feet per minute and the total free area in square feet.

Pitot Tube.[5] To measure the flow of large volumes of gas, a Pitot tube may be employed. The Pitot tube consists of two independent tubes, one of which is bent at right angles to the other in the simplest construction (Fig. 29). A more accurate device is one in which these tubes are joined concentrically and arranged to form an inverted L, which still permits them to act independently (Fig. 30). When either of these instruments is inserted into a gas stream, the tube facing the direction of flow measures the total pressure within the gas stream, consisting of a dynamic or kinetic pressure and a static pressure, while the tube perpendicular to the gas stream, or the tube with the static holes, measures the static pressure alone. The dynamic pressure is that pressure attributable to the impact of the moving gas. The static pressure is the pressure attributable to the presence of the gas itself by connecting the two tubes of the simple Pitot or the terminal arms of the L to a manometer, the difference in pressures may be noted. This difference in pressures is a measure of the speed with which the gas or air is traveling. The device measures this speed accurately only when the tube is properly pointed upstream.

If the total pressure is denoted by H, the dynamic pressure by h_k, and the static pressure by h_s then the pressure exerted at the opening pointed upstream is

$$H = h_k \pm h_s \tag{1}$$

depending upon whether there is a positive or negative pressure.

Fundamental hydrodynamic theory shows that in a stream of a moving fluid the pressure is greatest in the wide portions of the stream where the velocity is least, and is least in the narrow portions of the stream where the velocity is greatest. This relationship between pressure and velocity may be expressed by the equation for velocity of flow and the height of the water above an exit orifice as

$$v = \sqrt{2gh_w} \tag{2}$$

or

$$h_w = \frac{v^2}{2g} \tag{3}$$

where:

v = velocity in feet per second
h_w = height of water level above exit orifice
g = gravity constant = 32.2

The same relationship holds for air pressures and air velocities or for gas pressures and gas velocities, that is, the pressure created by a column of air of height h_a is proportional to the square of the air velocity, and

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[5] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1938).

$$h_a = \frac{v^2}{2g} \tag{4}$$

Because air and gas pressures are measured by water manometers or other types of manometer in which the pressures are expressed in inches of water, it is best to convert feet of air into inches of water.

$$h_a \times \text{density of air} = h_w \times \text{density of water} \tag{5}$$

$$h_a = \frac{\text{density of water}}{\text{density of air}} \times h_w \tag{6}$$

If the density of air is taken as 0.0749 pound per cubic foot and water as 62.4 pounds per cubic foot at 70° F., then, by substitution,

$$h_a = \frac{62.4}{0.0749} \times h_w = 833h_w \tag{7}$$

Thus the height of a column of air at 70° F. equivalent to 1 inch of water is 833 inches, or 69.4 feet, of air. By substituting this value and the value of the gravity constant in (4), we get

$$69.4h_w = \frac{v^2}{64.4} \tag{8}$$

Expressing the velocity of the air in feet per minute, we get

$$V = 4{,}009\sqrt{h_w} \tag{9}$$

To obtain the volume of air flow from the Pitot reading, the velocity must be related to the cross-sectional area of the duct. If Q represents the volume of air flowing in cubic feet per minute at an average velocity equal to *V* and *a* is the cross-sectional area of the duct in square feet,

$$Q = aV = 4{,}009a\sqrt{h_w} \tag{10}$$

Venturi Meter.[5] Another device used for the measurement of large volumes of gas flow is the Venturi meter. There are many variations of this instrument. They are all based on the principle, as is the Pitot tube, that the pressure and velocity head of a fluid are interchangeable. In the case of the Venturi meter this principle is reduced to the fact that the pressure of a gas on either side of a constriction in a pipe through which it is flowing is dependent upon the rate of flow. The rate of flow is increased by inserting in the pipe or conduit a fitting which converges to a minimum. The standardized Venturi meter consists of a converging and diverging duct connected by a narrow collar, as illustrated in Fig.

31. The diameter of the converging duct tapers down to $^1/_3$ of its original diameter at the minimum section in a distance of $2^1/_2$ diameters. The meter then diverges to its original diameter in a distance of $7^1/_2$ diameters. The length of the diverging taper minimizes loss attributable to the reduction in air velocity and eddying. The ratio dimensions of the standardized Venturi meter are given in Figure 31.

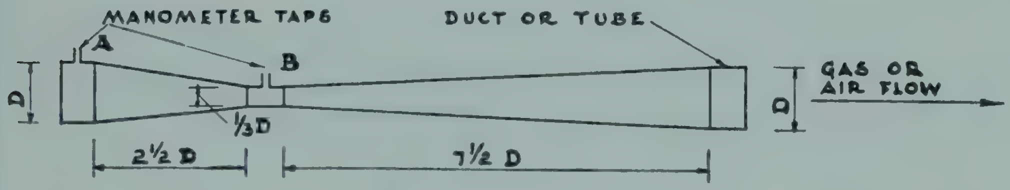

Fig. 31. Venturi meter.

The meter is tapped just before it begins to converge and at the minimum diameter. The taps are connected to a manometer. The difference in pressure created by the interchangeability of the velocity and static heads at *A* and *B* may be noted. It may be shown that the volume of air handled, *Q*, may be expressed by the formula

$$Q = \frac{21.2\, d^2_A \sqrt{h}}{[d^4_A/d^4_B - 1]^{1/2}} \tag{11}$$

where:
d_A = diameter of main in inches
d_B = diameter of minimum collar in inches
h = the difference in pressures

The Venturi meter is used mainly for the continuous measurement of large volumes of air flow or fluid flow in pipes and ducts. The manometers used in conjunction with the meter are often recording instruments. Venturi meters, as such, are not often used for the determination of the quantity of gas or air flow in sampling.

Orifice Meter. The orifice meter is a device that has at some point a standard capillary aperture. These orifices may be sharp-edged or bell-shaped. The tube with its capillary opening is connected to a manometer of some type. As the gas passes through the orifice, there is a difference in pressure created on one side of the orifice by the flow of gas with respect to the other side of the opening. This differential head is proportional to the square of the flow. The diminution in pressure between the downstream side and the upstream side of the orifice is registered by the connected manometer. The gauge may be graduated to read liters per minute directly, as in the gas flowmeter, or it may be graduated merely to read centimeters and millimeters. The corresponding volume may be read from a prepared graph. The graph is prepared from a formula

$$Q = \frac{13.4\, d^2_A \sqrt{h}}{[d^4_A/d^4_B - 1]^{1/2}} \tag{12}$$

where: d_A = diameter of tube in inches
d_B = diameter of orifice in inches

and the other symbols have the meaning previously indicated. The similarity to the formula for the measurement of volume of flow is clear. The energy losses are larger in the case of the orifice meter and therefore a greater correction must be made. The proportionality factor has a value of 0.60. An orifice meter having a hollow interchangeable stopper which is provided with four orifices of approximately $^1/_4$, $^1/_2$, 1, and 2 mm. diameter is commercially available.[6]

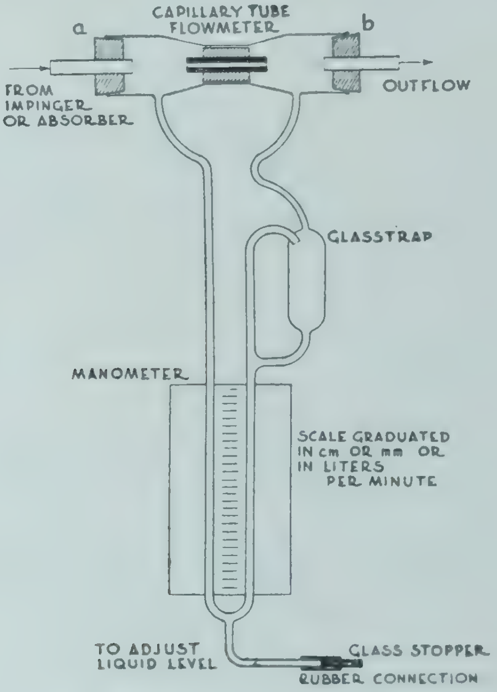
CAPILLARY TUBE FLOWMETER
a
b
FROM IMPINGER OR ABSORBER
OUTFLOW
GLASSTRAP
MANOMETER
SCALE GRADUATED IN cm OR mm OR IN LITERS PER MINUTE
TO ADJUST LIQUID LEVEL
GLASS STOPPER
RUBBER CONNECTION

Fig. 32. Gas flowmeter.

Orifice meters are widely used for estimating gas volumes in industrial-hygiene work. For dust determinations, these meters must be placed in the line after the absorbing, impinging, or collecting device rather than before the device, for the orifice may become obstructed by impinged dust and consequently fail to give a proper flow reading.

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[6] Corning Glass Wks., Corning, N. Y.

Gas Flowmeter. The gas flowmeter (Fig. 32) is an instrument that is based on the same principle as the Venturi meter. The constriction employed in the tube or conduit is a capillary tube. Some of these instruments consist of a tube *a* which can be connected to a tube *b* by replaceable capillary tubes (Fig. 32). On either side of the capillary tube there are taps in the tubes *a* and *b*, which can be connected to a manometer. The difference in pressure created on the upstream and downstream ends of the capillary is registered by the manometer, which may be graduated to read liters per minute. The gas flowmeter may be calibrated against

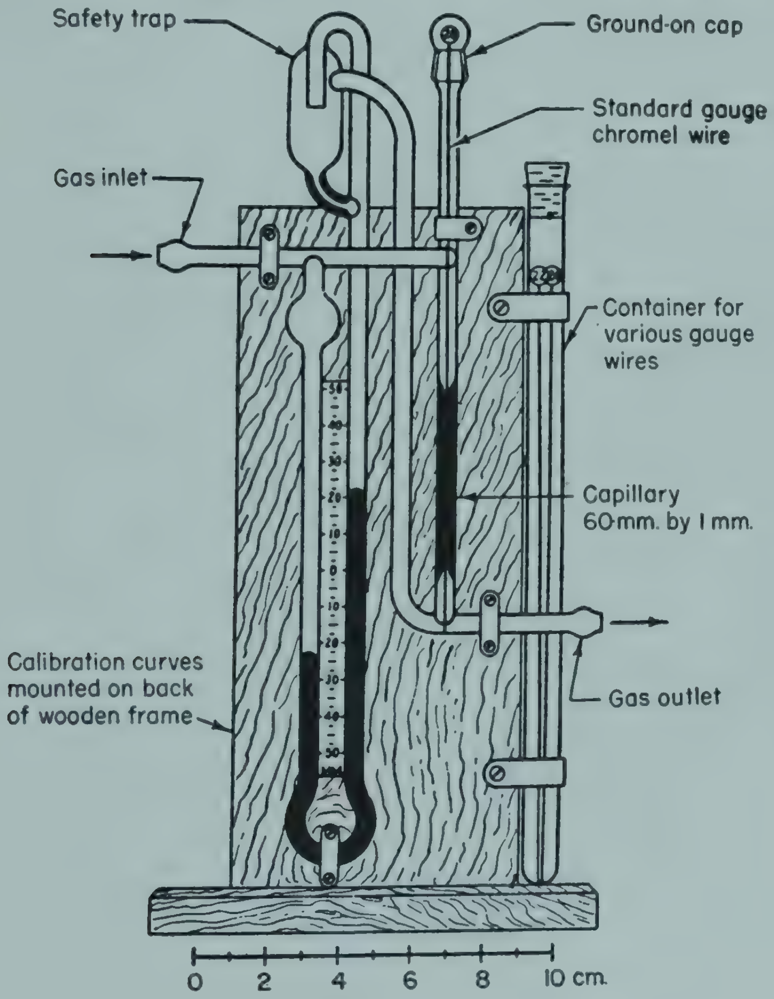
Safety trap
Ground-on cap
Standard gauge chromel wire
Gas inlet
Container for various gauge wires
Capillary 60 mm. by 1 mm.
Calibration curves mounted on back of wooden frame
Gas outlet
0
2
4
6
8
10 cm.

Fig. 33. Flowmeter.[7]

a direct-reading instrument such as a dry meter. Some instruments are equipped with a graph reading difference in height in arms of manometer against volume of gas passed. This instrument is fairly inexpensive, is one of the simplest to use, and is probably used more than any other device for measuring flow of gas in the field of industrial-hygiene chemistry. If used for dust determinations, it should, as with the orifice meter, be placed after the absorber in the sampling line.

Flowmeter with Variable Orifices.[7] The conventional capillary flowmeter is limited to a relatively narrow range of gas flows, depending upon the diameter and length of the capillary tube used. It is customary in many laboratories to use flowmeters provided with interchangeable capillaries, each of which may be attached to the flowmeter by means of one or two interchangeable ground connections.

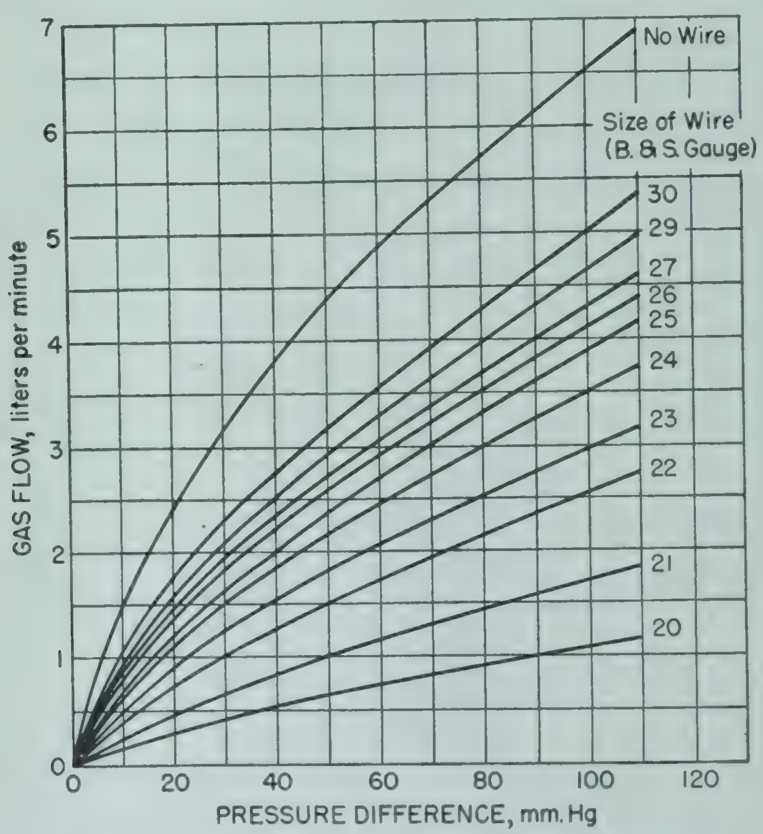

Fig. 34. Calibration curves for Bruun flowmeter.[7]

In the type of flowmeter shown in Figure 33, the vertical capillary tube is designed for the maximum gas flow expected. Wherever the flowmeter is to be used accurately for lower gas rates, the bore is decreased by inserting a corrosion-resisting alloy gauge wire such as chrome-nickel, Chromel, etc., into the entire length of the capillary. By using wires of different sizes, a flowmeter having a capillary 60 mm. long and 1.1 mm. in diameter can be used for accurate measurements of gas flow covering the complete range between 0.2 and 7.0 liters per minute. The calibration curves are shown in Figure 34. The approximate ranges of gas flows to which each wire is applicable when used in the capillary tube of the same dimensions is given in Table 1. This type of flowmeter can be readily cleaned by removing the gauge wire.

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[7] J. R. Bruun, *Ind. Eng. Chem., Anal. Ed., 11,* 655 (1939).

TABLE 1

Relation between Gas Flow and Pressure Difference for Various Wire Sizes[7]

B. and S. wire in 60- by 1.1-mm. glass capillary, gauge	Approximate gas flow, liters per minute		
	10 mm. Hg	60 mm. Hg	100 mm. Hg
20	0.2	0.7	1.1
21	0.3	1.2	1.7
22	0.4	1.7	2.6
23	0.5	2.1	3.0
24	0.6	2.4	3.5
25	0.7	2.7	3.9
26	0.8	2.9	4.2
27	0.9	3.1	4.3
29	1.0	3.3	4.7
30	1.1	3.6	5.0
None	1.5	4.8	6.5

Constant Flowmeter.[8] Hatch, Warren, and Drinker describe an ejector device that can be utilized as a constant flowmeter. Many industrial establishments have compressed air available. When compressed air is obtainable, the energy provided may be converted into suction as is the flow of water through a filter pump. This device uses about 50 cubic feet of free air when functioning and a constant rate is obtained with it regardless of the variation in air pressure, so long as this pressure is between the limits of 30 and 75 pounds per square inch. For an indicating device, a simple pressure gauge, connected to the compressed-air supply, is employed.

The constant flow in this meter is due to the fact that the pressure drop across the orifice ($p_1 - p_2$) is greater than the critical pressure, which for air is 0.53 p (where p_1 is the upstream and p_2 is the downstream pressure). Under this condition, the flow depends upon p_1 only, and since this remains constant, within the barometric-pressure range, the rate of air flow has a constant value. With a barometric pressure equal to 30 inches of mercury and the pressure loss through an impinger device equal to 2.9 inches, $p_1 = 27.1$ inches. To meet such a requirement $p_1 - p_2$ must be equal to or greater than 14.5 inches (that is, it must be equal to or greater than $0.53\ p$), and p_2 (absolute) must be less than 12.6 inches of mercury, that is, —17.4 inches of mercury gauge pressure. A suction in excess of this value is obtained with the aid of a No. 2 Hancock ejector, when the pressure in the air line is between 30 and 75 pounds. The orifice as designed by Hatch, Warren, and Drinker yields rates of flow from 28 to 29 liters per minute, which is equivalent to about 1 cubic foot per minute. The maximum variation is 3.5 per cent.

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[8] T. Hatch, H. Warren, and P. Drinker, *J. Ind. Hyg.*, *14*, 301 (1932).

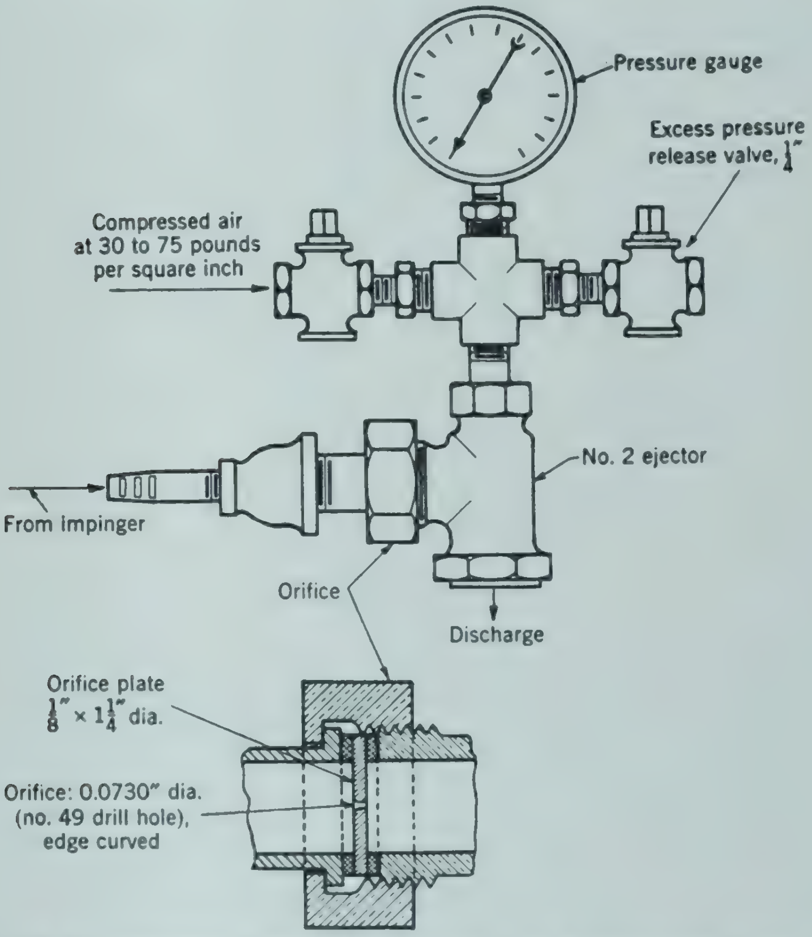
Pressure gauge
Excess pressure release valve, $\frac{1}{4}''$
Compressed air at 30 to 75 pounds per square inch
No. 2 ejector
From impinger
Orifice
Discharge
Orifice plate $\frac{1}{8}'' \times 1\frac{1}{4}''$ dia.
Orifice: 0.0730" dia. (no. 49 drill hole), edge curved

Fig. 35. Compressed air ejector flowmeter unit and detail of orifice and mounting.[9]

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[9] After T. Hatch, H. Warren, and P. Drinker, *J. Ind. Hyg.*, *14*, 301 (1932).

Capometer.[10] The capometer is an apparatus, used in Germany, which consists of a series of capillary tubes of different bores. The capillaries are independently connected to a manometer by means of stopcocks and the difference in pressure due to the flow through any one capillary is noted by the manometer. The capometer is really a type of Venturi meter or gas flowmeter that has a fixed set, instead of having replaceable capillaries.

Rotameter.[11,12] The rotameter is an apparatus which measures the velocity of flow of gas by the height to which a float is carried by a stream of gas. It consists of a glass tube mounted in a manner so that it can be leveled plumb. The gas enters at the lower end of the tube, and streams past and rotates a light float of clay, talc, or other material. The height to which the float rises depends on the velocity of the gas. The tube is graduated empirically for different gases. The theoretical aspects of rotameter flow rates for fluids are discussed by Whitwell and Plumb.[13] These devices are coming into increasing use as a means of measurement of air flow, particularly for investigational work on the toxicity of solvents. Devices are commercially available which cover a range of flow of 5.0 to 36,800 ml. per minute.

Thomas Electric Gas Meter.[14] The Thomas electric gas meter depends on the principle that if the specific heat of a gas is known, the amount of heat put into that gas by a coil—sufficient to maintain a given difference in temperature between two thermometers, one before and one after the coil—is a measure of the volume of gas flowing.

Thermo-anemometer.[15] The thermo-anemometer is an instrument capable of accurately measuring velocities of 10 to 6,000 feet per minute. It consists of an ordinary glass thermometer with an electric coil surrounding its bulb. Small dry cells furnish the heating current and the voltage is regulated by means of a rheostat. This auxiliary equipment is assembled in a small box. The equipment is commercially available.

The principle of operation depends upon the fact that the heated bulb cools off when exposed to air currents and the extent of cooling, as indicated by the difference of temperature between heated and unheated thermometers, varies with the air velocity. Readings are taken of the temperatures of heated and unheated thermometers and of the voltage used. The velocity is read off from a table or chart or it may be computed from an equation. By varying the voltage, any velocity within the range can be measured with accuracy.

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[10] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

[11] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

[12] N. H. Furman, *Scott's Standard Methods of Chemical Analysis,* Van Nostrand, New York, 1939.

[13] J. C. Whitwell and D. S. Plumb, *Ind. Eng. Chem., 31,* 451 (1939).

[14] G. Lunge and C. A. Keane, *Technical Methods of Chemical Analysis,* Van Nostrand, New York, 1924.

[15] C. P. Yaglou, *J. Ind. Hyg. Toxicol., 20,* 497 (1938).

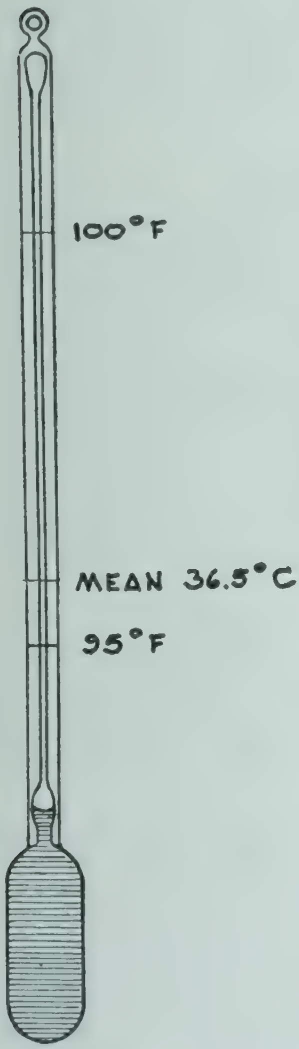

Fig. 36. Kata thermometer.

It can be used almost anywhere, in the open air or inside pipes, for measuring velocity or quantity of air flow. It is particularly useful for measuring air movement, in rooms or in front of exhaust hoods, that cannot be conveniently or accurately measured by other methods.

Kata Thermometer.[16–22] An instrument that can be used to measure air velocities but which is based on an entirely different principle from those already discussed, is the kata thermometer. This type of thermometer is generally called the kata. It was originally devised by Hill as a means of studying ventilation for body comfort. This thermometer was designed to simulate a human body and thus correlate the effects of temperature, relative humidity, and relative air movement. It is really an adaptation of the wet- and dry-bulb thermometer. It is so sensitive to air and gas movements that it can be used for velocity measurements.

The dry kata (Fig. 36) is an alcohol thermometer with a very large bulb and a stem which is about 20 cm. long. The stem has two main graduations, at 95° F. and 100° F. The alcohol is colored red for ease of vision. The reading of the dry kata gives the loss of heat due to convection, conduction and radiation. This reading can be related to air movement.[21]

To measure air velocity when the temperature is below 95°F., the kata is dipped into water at about 180°F. until the meniscus of the red-colored alcohol rises half-

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[16] L. Hill, *Med. Research Council, Spc. Rept. Series 32,* London.
[17] L. Hill, *Sunshine and Open Air,* London, 1924.
[18] L. Hill and A. Campbell, *Health and Environment,* London, 1925.
[19] T. C. Angus, *J. Ind. Hyg., 6,* 20 (1924).
[20] L. Hill, T. C. Angus, and E. M. Newbold, *J. Ind. Hyg., 10,* 391 (1928).
[21] J. Kerr, *The Air We Breathe,* London, 1926.
[22] C. P. Yaglou and K. Dokoff, *J. Ind. Hyg., 11,* 278 (1929).

TABLE 2
Comparison of Devices Used in the Measurement of Air Flow[23]

Device	Method of use	Range of air velocities or volumes which can be measured	Calculations based on	Accuracy obtainable	Skill required
Pitot tube	Used for measuring velocity head in ducts. Is pointed against direction of air flow.	200 ft./min. Upper limit not determined.	Formula: $V = 4009\sqrt{h_w}$ (ft./min.).	Depends on sensitivity of the manometer used.	Some. Location of tube is important.
Special Pitot	Used for measuring point velocities and velocity of air in ducts. Requires special mounting.	100 ft./min. Upper limit not determined.	Formula or curve. Device requires calibration against a standard pitot.	"	Considerable. The device is sensitive to direction of flow and requires careful mounting.
Anemometer	A vane instrument actuating a tachometer arrangement.	200 to 5,000.	Requires stop-watch timing. Device is direct reading, giving linear feet of air travel.	Requires a correction curve for high and low air velocities.	No skill required.
Kata thermometer	Bulb must be dried, and time of fluid fall or rise between 2 markings and air temperature are correlated with velocity.	15 to 500.	Requires a chart.	With careful use, the device is very accurate.	Radiant energy sources must be avoided.
Venturi	Fixed convergent and divergent tubes forming part of the duct system.	Can be built to handle any volume of air flow.	Formula: $Q = \frac{21.2d^2_A\sqrt{h}}{[d^4_A/d^4_B - 1]^{1/2}}$ d_A = diam. of main, in. d_B = diam. of throat, in.	Device is very accurate for volume determinations (0.5–5% error).	No skill required. Manometer scale can be made to read volumes directly.
Orifice	Orifice plate is fixed between two flanges in duct system.	Can be made to handle any volume of air flow.	Formula: $Q = \frac{13.4d^2_A\sqrt{h}}{[d^4_A/d^4_B - 1]^{1/2}}$ d_A = diam. of main, in. d_B = diam. of orifice, in	Device is very accurate when carefully calibrated.	"

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[23] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1938).

way into the safety bulb at the top of the thermometer. Then the bulb of the thermometer is rapidly and thoroughly dried and is held at the point where the velocity of air is to be measured. The time, T, in seconds, necessary for the alcohol to drop between the 100°F. and 95°F. markings is noted. This procedure should be repeated two or three times and the average time of temperature decrease observed and computed to avoid error. This time, T, divided into the factor number K, calibrated and given for each kata instrument, gives the cooling power, H, in millicalories per cm.^{2} per sec. That is

$$H = \frac{K}{T} \tag{12a}$$

If the temperature is above 100°F., in order to measure air velocity the kata must first be cooled below 95°F. by dipping the bulb into cold water. The bulb is then quickly and thoroughly dried and the time for the temperature to rise from 95°F. to 100°F. is noted. The heating power,—H, is calculated using the same formula (12a) but H is now considered negative.

The kata is not very accurate in the 85°F. to 100°F. range, because these temperatures are near its cooling range and air movements have little effect. A special high temperature kata, the blue kata, has been developed to overcome this defect.

Table 2 (page 71) gives a comparison of the properties of some of the devices used for the measurement of air flow.

B. MEASUREMENT OF QUANTITY IN GASES

It is well known that the volume of a gas alone gives no true measure of the quantity of matter present. In order to obtain the real quantity of gaseous matter present from the volumes obtained by the use of meters or of velocity instruments, the fundamental laws of gases must be applied. We have learned that the concentration of a sample of gas is proportional to the pressure it exerts. The fundamental considerations in the measurement of gases are the laws of Boyle and Charles.

1. Boyle's Law

The law of Boyle states that the volume occupied by the same sample of any gas at constant temperature is inversely proportional to the pressure. Mathematically stated,

$$P \propto \frac{1}{V} \tag{13}$$

Introducing a proportionality factor K, we have

$$P = \frac{K}{V} \qquad \text{or} \qquad PV = K \tag{14}$$

If, now, we were to change the pressure, we should, according to this law and the above relationships, obtain the expression

$$P_1V_1 = K \tag{15}$$

Dividing through (14) by (15), we get

$$PV = P_1V_1 \tag{16}$$

or

$$V = \frac{P_1V_1}{P} \tag{17}$$

This expression enables us to calculate a volume knowing the original volume, the original pressure, and the changed pressure, provided the temperature remains constant.

2. *Law of Charles*

The law of Charles gives the relationship between volume and temperature. This law states that the volume of a given sample of gas is directly proportional to the absolute temperature, the pressure remaining constant. Mathematically stated,

$$V \propto T \tag{18}$$

and introducing a proportionality factor

$$V = K'T \tag{19}$$

If, now, we were to change the temperature, we should, according to this law and the above relationship, obtain the expression

$$V_1 = K'T_1 \tag{20}$$

Dividing through (19) by (20), we get

$$\frac{V}{V_1} = \frac{T}{T_1} \tag{21}$$

or

$$V = \frac{V_1T}{T_1} \tag{22}$$

3. *Combined Law*

If the pressure and the temperature of a gaseous material change simultaneously, the volume is related to these changes by an expression known as the combined law, or the Boyle-Charles law. It can be seen by relating (13) and (18) that

$$V \propto \frac{1}{P} \text{ and } T$$

Multiplying the factors and introducing a proportionality factor, we get the well-known expression

$$V = \frac{kT}{P} \quad \text{or} \quad PV = kT \tag{23}$$

or

$$\frac{PV}{T} = k \tag{24}$$

If, now, we were to change the temperature and pressure of a gaseous system, we would get the expression

$$\frac{P_1V_1}{T_1} = k \tag{25}$$

and dividing through (24) by (25) we get the well-known mathematical expression for the combined law,

$$\frac{PV}{T} = \frac{P_1V_1}{T_1} \tag{26}$$

which for the purposes of calculating a volume from known data is generally expressed after multiplying, dividing, and collecting factors as

$$V = V_1 \times \frac{P_1}{P} \times \frac{T}{T_1} \tag{27}$$

4. *Standard Temperature and Pressure*

Some standard reference has to be accepted, if the measurement of gas volumes is to have meaning. This standard is known as the volume of a gas at "Standard Temperature and Pressure," generally abbreviated S. T. P. The standard temperature is 0° C. and the standard pressure is defined as the pressure of 760 mm. of mercury at 0° C. Hence to refer any volume of a gas to S. T. P., noting that the absolute zero of temperature is equal to —273° C., or conversely that 0° C. is equivalent to 273° K. (°K = degrees absolute), by substitution in (27) we obtain

$$V_{S.T.P.} = V_1 \times \frac{P}{760} \times \frac{273}{273 + t° C.} \qquad (28$$

5. *Dalton's Law*

In sampling and in analyses made with gases or air for industrial poisons, we know we are dealing with mixtures. There is another law which expresses the relationships of a mixture of gases. It is known as Dalton's law. This principle states that the pressure contributed by each component of a gaseous mixture is proportional to its concentration in that mixture and consequently the total pressure of the gas is the sum of the pressures of its components. There are two very important uses of this law in the field of industrial hazards. These are the corrections to be applied in the measurement of gas volume for the presence of water vapor and for the presence of residual gas in a partially evacuated vacuum gas collector.

In the case of measuring a volume of gas, say air, which is saturated with water vapor or which contains a known amount of water vapor, the actual volume of the gas is the volume measured, less the portion of the volume attributable to the water vapor. Expressed with respect to Dalton's law, the total pressure exhibited and measured is equivalent to the partial pressure of the gas and the partial pressure of the water vapor. That is, the pressure of the gas is equal to the total pressure less the partial pressure of the water vapor. The partial pressure of water, generally termed the aqueous tension, is known for a given temperature and may be obtained from the usual sources. By substitution of this correction in (28), we get

$$V_{S.T.P.} = V_1 \times \frac{P - P_w}{760} \times \frac{273}{273 + t^\circ\text{ C.}} \tag{29}$$

where P_w is the aqueous or the known vapor pressure of water at t° C. and the other symbols have the meanings previously defined.

6. Calculations

For specimen examples of the reduction of gases to standard temperature and pressure and for the corrections to be applied because of the presence of water vapor, the reader is referred to any text on the analysis of gases or on general chemistry.

The method for the calculation of the volume of a gas sampled by the method of a partial vacuum will, however, be detailed.

Let v_0 = effective volume of the bottle used for sampling. This is equivalent to the actual volume of the bottle less the volume of any absorbing or oxidizing solution if any is used.
b = barometric pressure
p_1 = partial pressure or residual pressure after evacuation

Then, after permitting the bottle to take the sample by coming to atmospheric pressure and the same temperature as before, we have by Dalton's law that:

$$b - p_1 = p_0$$

in which p_0 = the partial pressure attributable to the entering gas

Reducing the volume of the entering gas, v_2, to that occupied at barometric pressure, we have

$$v_2b = v_0p_0$$

and

$$v_2 = \frac{v_0p_0}{b}$$

and by substitution

$$v_2 = \frac{v_0(b - p_1)}{b} \tag{30}$$

Thus if the volume of the bottle, v_0, equals 5,000 ml. the barometric pressure, b, equals 750 mm. of mercury, and the residual pressure, p_1, equals 50 mm. of mercury, then by substitution

$$v_2 = \frac{5{,}000\ (750 - 50)}{750} = 4{,}666.7 \text{ ml.}$$

This volume is uncorrected for water vapor and is not reduced to standard conditions.

7. Gas Concentrations and Conversion Formulas

There are a number of different systems of expressing concentrations of substances in air. In industrial-hygiene chemistry the usual expressions are: parts of the contaminant per million of air; mg. of the contaminant per liter of air; per cent by volume of the contaminant in air; mg. of the contaminant per cubic meter of air (this expression is used mainly in expressing the concentrations of solids in air). All of these expressions are interchangeable. Thus,

$$\frac{\text{ppm.}}{10{,}000} \quad \text{per cent by volume}$$

or

$$1 \text{ per cent} = 10{,}000 \text{ ppm.}$$

In order to convert mg. per liter or any other weight per unit volume ratio to a volume per volume ratio, such as parts of vapor per million of air, use must be made of the gram-molecular volume relationship, namely, that the volume occupied by a gram-molecular weight of a gas at standard temperature and pressure (0° C. and 760 mm. pressure), is equal to 22.4 liters, or 24.45 liters at 25° C. and 760 mm. pressure. Thus:

$$\text{ppm.} = \frac{24{,}450 \times \text{mg.}}{M} \tag{31}$$

where M is the molecular weight of the substance and the other symbols have the meanings previously assigned. Suppose in a determination it was found that 1 mg. per liter of carbon disulfide was present and it was desired to convert this to parts of carbon disulfide per million of air, then by substitution in the above formula

$$\text{ppm.} = \frac{24{,}450 \times 1}{76.12} = 321.2 \text{ parts per million}$$

Or suppose the result had been calculated on the basis of parts per million and it was desired to convert to mg. per liter, then

$$\text{mg.} = \frac{\text{ppm.} \times M}{24{,}450} \qquad (32)$$

If one part per million was found, this is converted by substitution:

$$\text{mg.} = \frac{1 \times 76.12}{24{,}450} = 0.00311 \text{ mg. per liter}$$

For any multiple of 1 part per million or 1 mg. per liter, the result is obtained by simple multiplication. By use of Appendix Table 1,[24] which converts 1 mg. per liter into parts per million, and 1 part per million into mg. per liter, these calculations are greatly simplified.

To convert from mg. per cubic meter to parts per million, use formula (31) but divide the right-hand side of the equation by 1,000.

The expression cubic millimeters per cubic meter is also used occasionally; this is equivalent to parts per billion.

In order to obtain the quantity of a contaminant in an atmosphere that has been sampled by passing it through an absorbent, the analysis is made to find out the per cent of the contaminant in the aliquot part of the absorbing solution taken for analysis. From this result, the total quantity of toxic or hazardous material in the entire volume of the absorbing solution is calculated. From this value and the known volume of the air or atmosphere sampled, the amount of contaminant per unit of air or atmosphere can be computed.

Some factors for conversion of some units are the following:

(1) mg./liter × 28.32 = mg./cu. ft.
(2) mg./liter × 1000 = mg./cu. m.
(3) mg./cu. ft. × 35.314 = mg./cu. m.
(4) mg./cu. m. × 0.02832 = mg./cu. ft.

A convenient method of computation when the sampling rate is 0.1 cubic foot of air per minute, that is, 2832 ml. per minute is based on the relationship that:

$$1 \text{ ml. } 0.01\,N \text{ reagent} \approx 0.2445 \text{ ml. of monovalent gas at } 25\,^\circ\text{C. and } 760 \text{ mm.}$$

Then:

$$\frac{0.2445 \times 1{,}000{,}000 \times \text{ml. reagent}}{2832 \times \text{min.}} = \text{ppm. for gases of 1 hydrogen equivalent}$$

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[24] A. C. Fieldner, S. H. Katz, S. P. Kinney and Y. Henderson, *U. S. Bur. Mines, Tech. Paper 248* (1921).

which becomes:

$$\frac{86 \times \text{ml. reagent}}{\text{min.}} = \text{ppm. for gases of 1 hydrogen equivalent}$$

This becomes:

$$\frac{43 \times \text{ml. reagent}}{\text{min.}} = \text{ppm. for gases of 2 hydrogen equivalents}$$

These formulas have been used successfully for computing the concentration of the common acid gases and ammonia.

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CHAPTER IV

Absorbers and Absorbents

In most instances in studies, investigations, and analyses made in the field of industrial hazards, the substance to be estimated is present in such small quantity that a large volume of air must be sampled in order to obtain sufficient of the substance to ascertain its concentration with any degree of accuracy. There are a great many devices designed to give maximum absorption or adsorption when dusts, smokes, fumes, mists, or gaseous contaminants are passed into them. The absorbing fluid wets, dissolves, or reacts with the contaminant and thus retains the contaminant. The adsorbing material adsorbs the contaminant on its surfaces. It is important to have a proper evaluation of the efficiency not only of the absorber itself, but also of the absorbing fluid.

A. ABSORBERS

The laws governing the absorption of gases in liquids are the laws governing heterogeneous equilibria and reaction velocity in heterogeneous systems. In the simplest case, where a gas dissolves in the absorbing medium and does not react with it, Henry's law applies: the concentrations of any single molecular species in two phases at equilibrium bear a constant ratio to each other. However, in those systems in which the gas or other substance absorbed forms a different molecular species in or reacts with the absorbing medium, Henry's law must be modified by combination with the mass law or by taking into account the association or dissociation of the substance absorbed.

In many instances these considerations are merely theoretical, as, for instance, in the absorption of hydrogen chloride by water, for the partial pressure of hydrogen chloride in aqueous solutions containing up to 250 g. per liter is practically negligible. But in other instances the partial pressure of the gas to be absorbed in the atmosphere above the absorbing fluid cannot be neglected. By the use of multiple absorbers, the partial pressure of the gas in the air stream can be reduced to a negligible amount.

It is important to choose the proper absorbing medium. Thus, for example, Nordlander[1] points out that where aqua regia is used as the absorbent for mercury vapor, errors may result because a white coat of mercuric chloride forms around a drop of mercury and protects it from further solution. Nitric acid alone is a better absorbent.

Solubility and insolubility of a contaminant in an absorbing medium are not the only criteria. Thus, long sampling time may lead to erroneous results where the contaminant may be oxidized by the aeration stream, as in the case of low concentrations of formaldehyde.

1. *Efficiency*

The efficiency of an absorber, absorbent, adsorbent, etc., may be defined as the ratio of contaminant trapped by the device or substance to the total amount of contaminant present in the air stream.[2] The percentage efficiency is equal to the parts per million of contaminant in the entering gas minus the parts per million of the contaminant in the effluent gas divided by the parts per million of contaminant in the entering gas multiplied by 100:

$$\%\ \text{Efficiency} = \frac{\text{ppm. entering gas} - \text{ppm. effluent gas}}{\text{ppm. entering gas}} \times 100$$

Efficiency depends on a number of factors, such as the design of the absorber device, the rate of flow of the sampling stream, the absorbing solution, absorbent or adsorbent used, the temperature, and other factors. Increasing the number of absorbers increases the efficiency of absorption. The theoretical aspects of absorption in nonreacting media are discussed by Elkins and his co-workers.[3] The velocity of reaction at a gas-liquid interface is discussed by Taylor.[4]

The efficiency of an absorber or sampling device should be tested before it is adopted for field use.[5] This may be done in a number of ways:

1. By the use of a gas-tight compartment, chamber, or tank into which it is possible to introduce known concentrations of a vapor; or a cylinder filled with a synthetic gas mixture for reference.

2. By the comparison of the results obtained with a device under test with those of a device known to be accurate.

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[1] B. W. Nordlander, *Ind. Eng. Chem., 19,* 522 (1927).

[2] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem., 11,* 519 (1919).

[3] H. B. Elkins, A. K. Hobby, and J. E. Fuller, *J. Ind. Hyg. Toxicol., 19,* 474 (1937).

[4] H. S. Taylor, *Treatise on Physical Chemistry,* Van Nostrand, New York, 1931.

[5] *Am. Pub. Health Assoc. Yearbook 1939–40,* p. 92.

3. By the introduction of a known quantity of material into the sampling train.

4. By noting the amount of material trapped in a second unit of the absorption train when a single absorber is being tested. (This method sometimes leads to erroneous results. Paluch[5] found that a second impinger only collected a small part of the sulfur dioxide and hydrogen sulfide which passed through the first impinger without being trapped. Littlefield and his co-workers[6] found more lead fume trapped in a second impinger than in the first impinger of a sampling train.)

5. In addition, to test the efficiency at different sampling rates, two absorbers of the same type may be tested in parallel, the rate of flow through one of them adjusted to be faster than through the other.

2. *Trapping Devices*

It is necessary to choose the absorption device used for a particular purpose with care, for upon the absorption or adsorption device used may depend the accuracy of the test. The devices may, for the sake of convenience, be placed into three main groups:

(1) U-tubes and bulbs in which the contaminant is trapped by an adsorbent or absorbent, generally of a solid nature, such as activated charcoal, silica gel, Ascarite, soda lime, Dehydrite, impregnated porous materials, or glass wool or cotton wet with some active reagent. The devices may be simple U-tubes or bulbs or even more elaborate devices with interchangeable glass ground connections and stoppers.

(2) Devices which depend upon the washing of the incoming gas stream to absorb the contaminant. This group may be subdivided into four subgroups:

- (a) The simple gas-wash bottles or absorbers, in which the length of travel is equivalent to the height or length of the absorbing liquid in the device.
- (b) The spiral devices, in which the length of travel is many times greater than the height or length of the apparatus.
- (c) Devices equipped with some dispersion mechanism, such as a fritted-glass plate or an Aloxite distributor. These devices are often termed bubblers.
- (d) Devices that increase the length of travel by increasing the

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[6] J. B. Littlefield, F. L. Feicht, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3401* (1938).

direct path traversed. These types are in reality multiple simple absorbers combined into one apparatus.

(3) Devices which increase the path by means of baffles and so are, in reality, scrubbing rather than merely washing devices.

One cannot state dogmatically that any one particular type of absorber is to be preferred for industrial hygiene work because each absorber has some particular feature which lends itself to best advantage in a given method. There are some absorbers that lend themselves to more general use than others. In the description which follows of the more common types of absorbers that are employed in the chemical determination of contaminants in air, the particular advantage of each type will be mentioned. Such characteristics as ease of washing, ease of recovery of the absorbed material, durability, adaptability, and expense are all to be considered in the selection of adequate absorbers.

a. U-Tubes and Bulbs

U-tubes or at times bulbs and simple tubes are used principally when it is desired to weigh the material absorbed or adsorbed or when it is necessary to liberate the trapped material for further analytical treatment. They are also generally used when the contaminant to be sampled is trapped by freezing, as these devices lend themselves more readily to immersion in a freezing bath. A typical illustration of this use is the method for the determination of benzene described on page 538. In this method the benzene is trapped by freezing in a U-tube packed with solid carbon dioxide, then is volatilized and refrozen in a test vessel. As examples of the use of U-tubes that are weighed before and after sampling, see the general methods for the determination of solvent vapors as detailed in Chapter XII, and the procedure for *p*-dichlorobenzene, page 596.

One can include in this group the many combustion absorption bulbs designed for holding solid absorbents, such as Ascarite,[7,8] a special sodium hydroxide-asbestos absorbent mixture; Dehydrite, magnesium perchlorate trihydrate, $MgClO_4.3H_2O$[9,10]; Anhydrone, anhydrous magnesium perchlorate; Desicchlora, anhydrous barium perchlorate; soda lime, a mixture of calcium oxide and sodium hydroxide, the sodium hydroxide content ranging from 5–20 per cent, etc. These devices are used in the

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[7] J. B. Stetser and R. H. Norton, *Iron Age, 102,* 443 (1918).

[8] J. S. Buck, *Ind. Eng. Chem., 18,* 1321 (1926).

[9] G. F. Smith, M. Brown, and J. F. Ross, *Ind. Eng. Chem., 16,* 20 (1924).

[10] H. H. Willard and G. F. Smith, *J. Am. Chem. Soc., 44,* 2255 (1922).

trains designed for the determination of carbon in steeel and in organic chemicals. They can also be used for other trapping purposes. Among these may be mentioned the absorption bulbs of Turner,[11] Midvale, Fleming, Vanier, and others. Illustrations of these devices can be found in almost any laboratory-equipment catalogue.

b. Washing Devices

Washing Bottles and Bulbs. There are many different types of these gas-washing devices. In the simple type the gas is permitted to enter at some point and it can find its way out only by traversing the length of the absorbing liquid. In these types the length of travel of the gas bubble is practically equivalent to the height or length of the absorbing liquid. Among those that may be taken as representative of this group are the Drechsel (Fig. 37) and Allihn types. Some others are the Drehschmidt petticoat inner-tube absorbing cylinder, the Fieldner[12] petticoat type, Petri tubes,[13] Habermann, Muencke, Bunsen, etc., absorption gas-washing bottles.

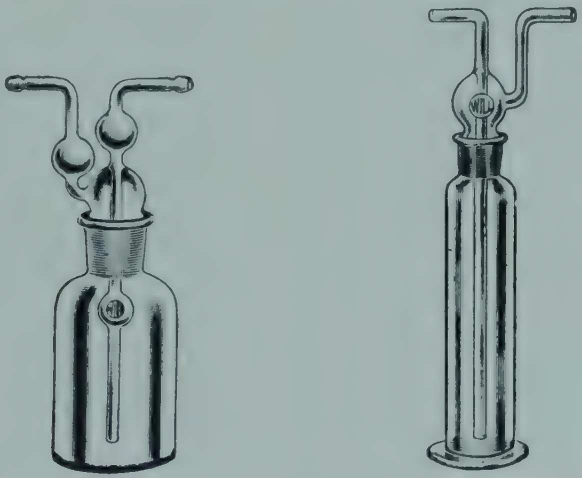

Fig. 37. Drechsel high- and low-form gas-washing bottles. (*Courtesy Will Corporation*)

These devices are not particularly efficient absorbers and generally must be connected in multiples for maximum efficiency. They do, however, have certain advantages over other, more efficient absorbers. Thus in those instances in which a precipitate is to be recovered—for example the formation of diphenylurea from aniline and phosgene in the test for phosgene, detailed on page 390—the Drehschmidt petticoat and Drechsel types are to be preferred, for they can be washed out readily and the precipitate cannot lodge in inaccessible places. They also can be cleaned more readily than other types and can be used as direct titration vessels.

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[11] W. D. Turner, *Ind. Eng. Chem., Anal. Ed. 3,* 63 (1931).

[12] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem., 11,* 519 (1919).

[13] A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases,* Service to Industry, Hartford, 1936.

Included among the simple absorbing devices is the impinger, described in detail in Chapter V. It differs somewhat in principle, however, in that the forward motion of a particle is momentarily arrested by impingement against a baffle, thus assisting the washing action.

Spiral and Helical Devices. The spiral absorption devices, in which the length of travel is considerably greater than the height or length of the absorbing liquid itself, are among the most efficient absorbers of the single type. In such equipment the gas is forced to travel in a helical path either in a tube or because of a helical baffle arrangement, so that the gas is in a washing fluid for from 5 to 10 times the length of travel of the simple washing type. The stream of gas bubbles forces some of the liquid up the incline, which in turn rotates the gas bubbles as they themselves travel up the helical path. This gives an added washing effect. Some of these devices are illustrated in Figures 38 and 39.

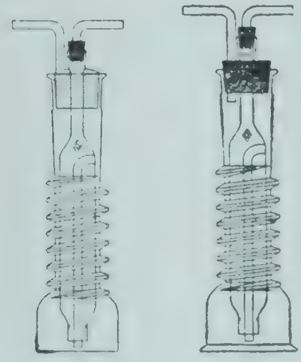

Fig. 38. Spiral gas-washing bottles. (*Courtesy Chicago Apparatus Corp.*)

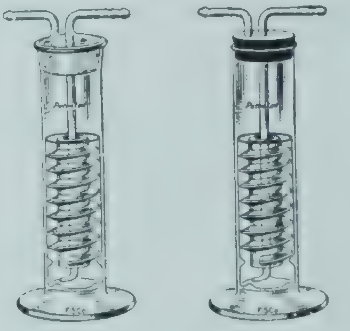

Fig. 39. Milligan gas-washing bottles. (*Courtesy Chicago Apparatus Corp.; Fisher Scientific Co.*)

Rhodes and Rakestraw,[14] testing the efficiency of gas-washing bottles, found that the Friedrichs[15,15a] spiral gas-washing bottle was the most efficient for the absorption of carbon dioxide by a sodium hydroxide solution. A spiral type of absorber that was efficient for the absorption of carbon dioxide and contained only a relatively small volume of alkaline absorbing medium (30 ml.) as compared with the Friedrichs and Milligan gas-washing bottles is described by Martin and Green.[16]

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[14] F. H. Rhodes and D. R. Rakestraw, *Ind. Eng. Chem., Anal. Ed., 3,* 143 (1931).

Other spiral-type gas-washing bottles are those of Pearce and Roberson,[17] Corson,[18] Weaver and Edwards,[19] and Keller.[20] Smyth[21] describes one which is designed to hold only a small volume of nitrating acid for trapping benzene, Fig. 107.

Dispersers and Bubblers. It has been shown, however, that besides the length of travel in which a gas and liquid are in contact with each other, the size of the gas bubbles distributed within the liquid absorbing medium is also of decided importance.[22,23] The size of the entrance orifice of a single tube may be used to regulate the size of the entering bubble, but such a constriction may impede the flow of the gas stream. In order to achieve adequate dispersion without diminishing efficiency or increasing flow resistance to a considerable extent, use may be made of sintered- or fritted-glass disks and thimbles. One of the most important applications of glass filters is in securing intimate contact between gaseous and liquid phases. The early bibliography of this subject has been reviewed by Prausnitz.[24]

Fritted-glass disks are made of ground and sifted glass powder sintered in suitable molds, without any binder, into porous plates, etc., of glass, which may subsequently be fused into any desired shape of solid glass of the same coefficient of expansion. By choosing a particular type of glass, any quality of chemical or temperature resistance may be obtained. Ordinary soft glass or Pyrex or even fused quartz may be used and joined to glass of a different composition by the use of special joining glasses. Figure 40 shows an absorber and tube fitted with fritted disks.

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[15] J. Friedrichs, *Z. angew. Chem.*, *32*, 252 (1919).

[15a] F. Friedrichs, *Chem. Fabrik*, *4*, 203 (1931).

[16] W. Martin and J. R. Green, *Ind. Eng. Chem., Anal. Ed.*, *5*, 114 (1933).

[17] P. H. Pearce and E. C. Roberson, *Chemistry & Industry*, *55*, 543 (1936).

[18] B. B. Corson, *Ind. Eng. Chem., Anal. Ed.*, *10*, 646 (1938).

[19] E. R. Weaver and J. D. Edwards, *Ind. Eng. Chem.*, *7*, 534 (1915).

[20] K. Keller, *Chem.-Ztg.*, *47*, 506 (1923).

[21] H. F. Smyth, *J. Ind. Hyg.*, *11*, 338 (1929).

[22] A. Sieverts and S. Halberstadt, *Chem. Fabrik*, *3*, 201 (1930).

[23] S. Halberstadt, *Ind. Eng. Chem., Anal. Ed.*, *4*, 425 (1932).

[24] P. A. Prausnitz, *Ind. Eng. Chem., Anal. Ed.*, *4*, 430 (1932).

Other devices are illustrated by Prausnitz.[24] Indeed, almost any washing bottle, such as the Drechsel or Petri types, may be equipped with such sintered-glass distributors and thereby have its efficiency greatly improved.

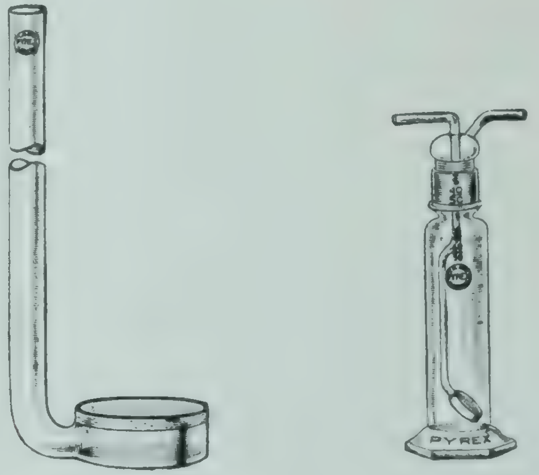

Fig. 40. Fritted-glass-disk bubblers. (*Courtesy Corning Glass Works*)

It is well to note that the size of the bubbles is a function not only of the diameter of the orifice from which it emerges but also of the surface tension of the liquid surrounding the disperser.[25] Thomas[26] developed a continuous carbon dioxide recorder that had an absorber with a fritted porous plate in which dispersion of gas bubbles was obtained not only by the use of the porous plate but also by the addition of a higher alcohol, like butyl alcohol, which acted as a surface-tension depressant and thus reduced the size of the entering bubbles. The butyl alcohol also produced a froth, which served to increase the time of contact of the gas with the liquid. This made an apparent increase in the volume of the absorbing liquid of 2 or 3 times, for the tiny bubbles had to circulate and recirculate within the froth before they were able to emerge.

Fritted-glass-disk bubblers in various porosities are commercially available. Directions for the preparation of fritted disks particularly for specialized uses may be found in the literature.[27-30] For most in-

[25] O. C. Ralston and C. G. Maier, *U. S. Bur. Mines, Bull. 260* (1927).

[26] M. D. Thomas, *Ind. Eng. Chem., Anal Ed., 5,* 193 (1933).

[27] P. L. Kirk, R. Craig, and R. S. Rosenfels, *Ind. Eng. Chem., Anal. Ed., 6,* 154 (1934)

[28] W. F. Bruce and H. E. Bent, *J. Am. Chem. Soc., 53,* 990 (1931).

[29] H. W. Stone and L. C. Weiss, *Ind. Eng. Chem., Anal. Ed., 11,* 220 (1939).

[30] R. D. Cool and J. D. Graham, *Ind. Eng. Chem., Anal. Ed., 6,* 479 (1934).

dustrial-hygiene work the porosity designated as coarse is preferred. The customary rate of sampling is 0.5 to 1 liter per minute. Too fine a porosity increases the need for greater power to drive the air stream through the device. This in turn requires bulkier apparatus.

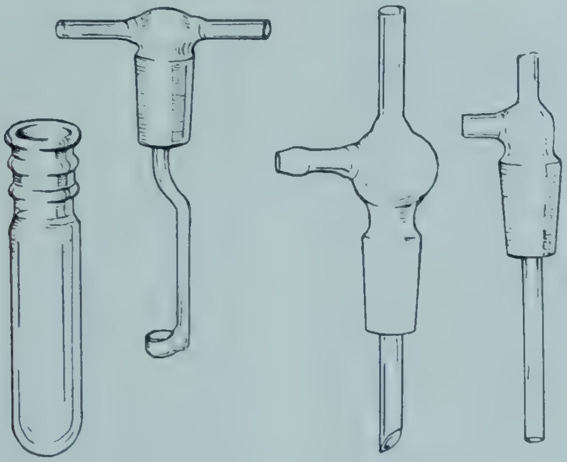

Fig. 41. Midget all-glass fritted-disk bubbler.

The midget impinger (Chapter V, Section C7d) has been modified to make it a fritted-disk bubbler (Fig. 41). By means of these modifications it can be used for the collection of vapors with a small volume of aqueous and nonaqueous reagents, at a sampling rate of 1 to 3 liters per minute.

Apparatus of New York State Industrial Hygiene Laboratory.[31] The New York State Division of Industrial Hygiene laboratory decided to standardize their absorbers by using the following types for most of their sampling requiring absorption. One device (Fig. 42) consists of a 250-ml. glass-stoppered Drechsel wash bottle with standard taper ground-glass connections at the entrance and exit tubes, equipped with glass hooks sealed at the connections as an aid in keeping joints tight when several bottles are used in series. A sintered-glass disk with No. 1 porosity (German designation), which corresponds very closely to porosity B of disks manufactured in the United States, is fused to the end of the gas-entrance tube near the bottom of the bottle. About 100 ml. of absorbing fluid is used in each bottle. Two or more of these devices can be connected in series without the use of any rubber because of the standard taper connections. This apparatus is used for those estimations in which contact between the air to be analyzed, or the medium used for absorption, and rubber, metal, or cementing materials is to be avoided.

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[31] S. Moskowitz, J. Siegel, and W. J. Burke, *N. Y. State Ind. Bull. 19,* 33 (1940).

For use with small volumes of liquids, a smaller all-glass absorber (Fig. 42) is made of one piece, about 7 inches high by 1 inch in diameter.

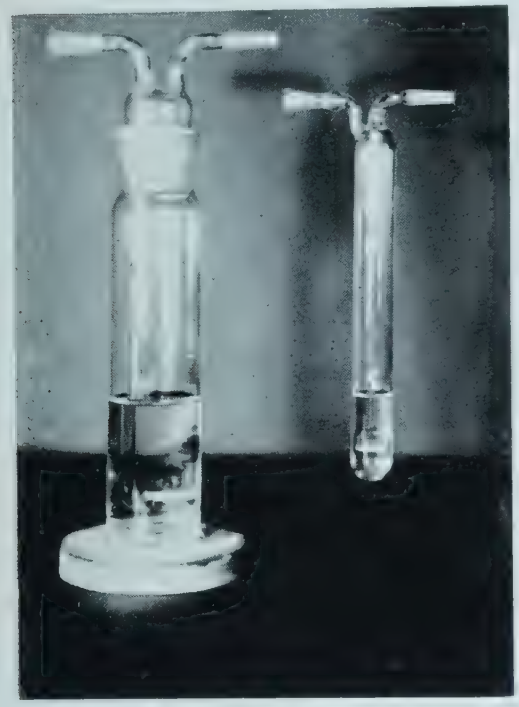

Fig. 42. Large and small all-glass absorbers.

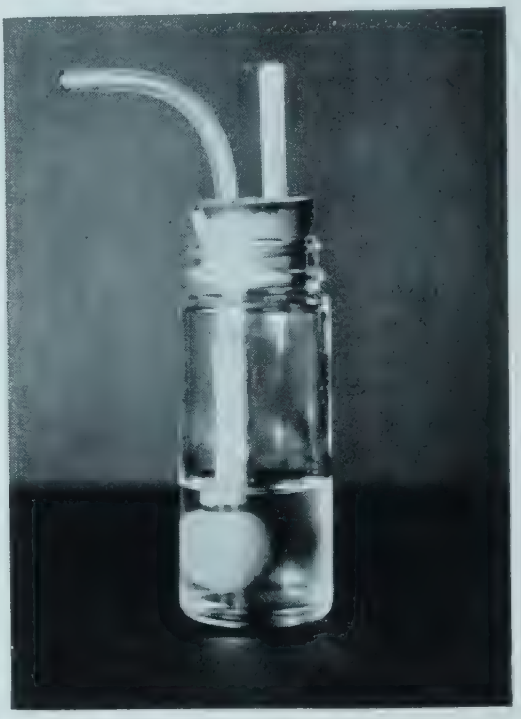

Fig. 43. Absorber with Aloxite gas distributor.

(Courtesy Div. Ind. Hyg., N. Y. State Dept. of Labor)

The ground-glass joints at the ends of the gas-entrance and -exit tubes are of standard taper but of smaller dimensions than those on the larger all-glass apparatus. Because the sintered-glass disk is smaller in diameter in this device, it is best to reduce the rate of gas flow through this absorber to about two-thirds the rate through the larger apparatus. From 10 to 15 ml. of absorbing liquid is sufficient for this type.

Another type consists of a glass vial about 4.5 inches high by 1.75 inches outside diameter (Fig. 43). This vial is fitted with a two-hole rubber stopper. An Aloxite stone is attached to the gas-entrance tube by means of cement or by a rubber connection fitted to the metal nipple with which some of these stones are supplied. The Aloxite stone acts as the gas distributor. About 35 ml. of absorbing liquid is used in each vial and as many as necessary are connected in series. This type of apparatus is relatively inexpensive and has the additional advantage of flexibility between absorbers. It may be used in many instances, but not where the presence of metal, rubber, or cementing material will interfere with the analysis.

The Drechsel washing bottle described above may be fitted with an Aloxite stone with the aid of cement instead of being equipped with a fritted-glass distributor. Errors resulting from rubber connections in gas-washing bottles not equipped with standard taper connections may be eliminated or minimized by carefully squaring the ends of the absorbers and arranging glass-to-glass connections held in place with rubber tubing as described in Chapter II (Fig. 6). In these instances the cementing material must then be selected so that it will cause no interference with the absorption and analysis. Litharge and glycerol, magnesium oxychloride, and bakelite resin are a few of the cements which may be employed for this purpose. This apparatus is less expensive and has most of the advantages of the all-glass apparatus.

In using these pieces of equipment for the absorption of gases from industrial air, it has been found necessary to use only two absorbers in series when the air is run through at a rate of 30 liters per hour. The length of time required for sampling depends on the concentration of contaminants encountered and on the precision and accuracy of the chemical analytical method. The usual sampling time varies from 20 minutes to 2 hours. With the all-glass apparatus, an all-glass flowmeter with a standard taper connection to fit those of the washing bottles may be used on the downstream side of the sampling train; any flowmeter connected with rubber tubing may be used on the upstream side. In the latter case the flowmeter must be calibrated to read in terms of flow of air at atmospheric pressure, although at that point the gas passing through the flowmeter is at a pressure somewhat below atmospheric. The drop in pressure through each sintered-glass disk is about 1 inch of mercury when the rate of air flow is 30 liters per hour. The absorption devices using Aloxite stones are used with a flowmeter on the downstream side. The drop in pressure across each stone is about 3 inches of mercury with an air flow of 30 liters per hour.

The Laboratory of the Division of Industrial Hygiene of New York State uses the all-glass device for the estimation of hydrogen sulfide, carbon disulfide, both gases simultaneously, acid vapors and mist, and ammonia. The apparatus containing an Aloxite-stone gas disperser is used for the estimation in air of methyl alcohol, other alcohols, formaldehyde, and other aldehydes and phenols.

Harrold Mist and Gas Collector. One of the disadvantages of fritted-disk bubblers as a means of sampling gases and vapors is the channeling of the air stream through a relatively small number of pores in the fritted disk, with subsequent decrease in the efficiency of absorption. Harrold[32] overcomes this by using the method of the common impinger (page 133) to baffle the air flow and thus distribute it evenly, with the aid of a small plenum chamber, through the fritted disk. With this device efficiencies of over 95 per cent were obtained in the collection of sulfur dioxide, sulfur trioxide, carbon dioxide, hydrogen sulfide, and hydrogen chloride and over 97 per cent in the collection of hydrochloric acid and chromic acid mists.

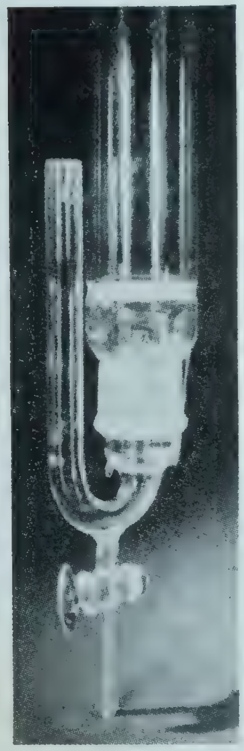

Fig. 44. Harrold mist and gas collector. (*Courtesy Production Equipment Co.*)

Multifold Absorbers. The length of travel of a gas through an absorbing solution may be increased in ways other than by spiraling the path. One of the older forms is Lunge's or Meyer's ten-bulb absorption tube. Another is the bulb tube designed by Thomas[33] and fitted with a fritted disk. Still another arrangement is a multiple absorber that can be filled and emptied as a single unit.[34] These devices are in reality multiple absorbers built into one unit instead of being attached mechanically and then separated for filling, rinsing, washing, etc. They have the advantage that they are more efficient than a single absorber, for the most efficient way to absorb vapors in nonreacting liquids is to use a number of absorbers in series.

The well-known potash bulbs, illustrations of which can be seen in most laboratory-equipment catalogues, are also types of devices which are multifold absorbers.

Lift-Pump Gas Absorber. As has been stated before, intimate contact of a gas with the absorbing liquid is one of the important prerequisites of satisfactory absorption of a contaminant. The principle of the air-lift pump was used by Nichols[35] in designing a device to absorb sulfur dioxide from air. Greater contact with an iodine-absorbing solution was achieved by causing a turbulence in an inner tube of the apparatus.

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[32] C. G. Harrold, Production Equipment Co., Detroit 2, Mich.

[33] M. D. Thomas, *Ind. Eng. Chem., Anal. Ed.*, *5*, 193 (1933).

[34] H. B. Elkins, A. K. Hobby, and J. E. Fuller, *J. Ind. Hyg. Toxicol.*, *19*, 474 (1937).

c. Scrubbing Devices

These absorption devices increase the path of travel of the gas stream by means of baffles and so exert a scrubbing effect rather than merely a washing effect, as the incoming gas stream is completely broken up in finding its way out of the devious path set up by the baffles. These types generally consist of a glass tube filled with glass beads wet with the absorbing medium. The incoming gas stream is admitted in such a manner that it can only find its way out by passing through the maze presented by the glass beads or short glass rods. These designs are very often used where only a very small amount of absorbing solution is permissible or desired. Among the devices in this group that may be mentioned is the one Shaw[36] used for the determination of nitric oxide in coke-oven gas; the absorber for the microdetermination of benzene[37] and toluene[38] (Fig. 106); the absorber used in the sulfur lamp-apparatus method for the determination of chlorinated hydrocarbons (Fig. 117); absorbers used in combustion methods for the determination of chlorinated hydrocarbons[39,40] (Figs. 111 and 113); that of Barrett[41] for the estimation of trichloroethylene (Fig. 118); and that of Petersen and Radke[42] for the determination of acrylonitrile (Fig. 102A).

The siphon section of a Soxhlet extractor filled with glass beads, which is placed in the sampling train so that the gas to be tested passes through the siphon tube before reaching the beads, can also be used as a scrubbing device. Still another variation of these devices may be made from a tube similar to an Ostwald viscosimeter or one of its modifications, the wide section of which is filled with glass beads. The device is placed in the sampling line so that the incoming atmosphere passes through the capillary section first.

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[35] N. S. Nichols, *U. S. Pub. Health Repts., 53,* 538 (1938).

[36] J. A. Shaw, *Ind. Eng. Chem., Anal. Ed., 6,* 479 (1934).

[37] H. H. Schrenk, S. J. Pearce, and W. P. Yant, *U. S. Bur. Mines, Rept. Invest. 3287* (1935).

[38] W. P. Yant, S. J. Pearce, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3323* (1936).

[39] B. D. Tebbens, *J. Ind. Hyg. Toxicol., 19,* 204 (1937).

[40] C. K. Drinker, M. F. Warren, and G. A. Bennett, *J. Ind. Hyg. Toxicol., 19,* 283 (1937).

[41] H. M. Barrett, *J. Ind. Hyg. Toxicol., 18,* 341 (1936).

[42] G. W. Petersen and H. H. Radke, *Ind. Eng. Chem., Anal. Ed., 16,* 63 (1944).

3. Freezing Traps

In addition to the use of U-tubes and bulbs as freezing traps, there are devices which are specially designed for this purpose. One of these devices is illustrated in Fig. 45. It fits readily into a Dewar flask or thermos bottle and so can easily be immersed in a fluid freezing mixture.

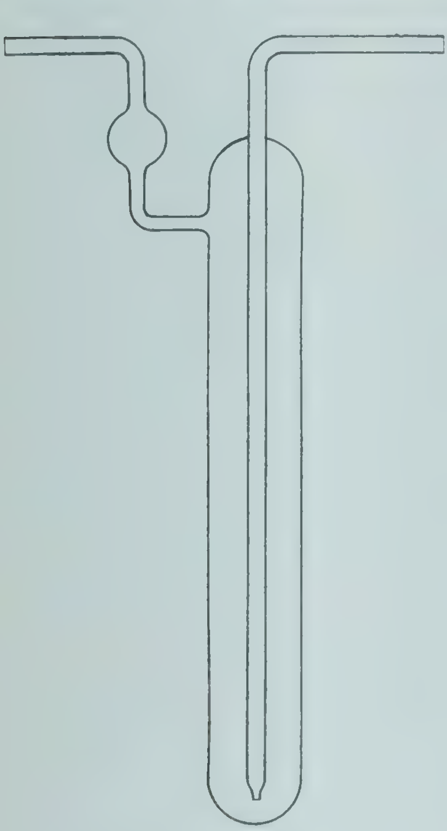

Fig. 45. Freezing trap.

Carbon monoxide, mercury, benzene, *p*-dichlorobenzene, and refrigerants and solvents, in general, may be estimated by freezing methods.

In using a freezing trap either for the collection of the vapor or for estimation by weighing, one must consider the possible formation of a fine mist, which will pass out of the tube without condensing, and the possible freezing of water vapor, causing a clumping within the collecting tube and thus completely obstructing the flow of air. Thus bromine cannot be efficiently trapped using a 16-mm. U-tube in a dry ice-methanol freezing mixture.[43]

4. Heated Traps

Heated trapping devices are generally quartz, heat resistant glass, or metal tubes which are heated and in which some contaminant of the air stream is deposited because of decomposition. Examples are the deposition of an arsenic or antimony mirror in a heat resistant glass tube by heating a stream of gas containing arsine or stibine. Another is the decomposition of iron pentacarbonyl and nickel tetracarbonyl by heat with the deposition of the iron or nickel in the heated tube. Generally a silica or heat resistant glass tube is used at a red heat temperature for this purpose. Chlorinated hydrocarbons are also decomposed by passing them through heated tubes but in this instance there is no deposition in the tube and so it does not act as a trap. The chlorides formed must be caught by some other means.

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[43] F. H. Goldman and J. M. DallaValle, *U. S. Pub. Health Repts., 54,* 1728 (1939).

5. *Classification of Absorbers Used for Gases and Vapors*

This classification follows the recommendations of the American Public Health Association.[44]

(1) The following gases and vapors are readily soluble in the absorbing agent commonly employed (see Table 3) and can be absorbed with success in fritted-glass bubblers, and possibly in the impinger:

Acetic acid
Acetone
Ammonia
Hydrochloric acid
Hydrofluoric acid
Nitric acid
Methyl alcohol
Amyl acetate
Butyl acetate
Carbon disulfide
Formaldehyde
Hydrogen cyanide

(2) The following gases are less soluble and more care must be taken or absorption will not be sufficiently complete. One or more fritted glass bubblers in series are recommended.

Sulfur dioxide
Sulfur monochloride
Hydrogen sulfide
Phosgene
Phosphine
Phosphorus chlorides
Carbon dioxide
Chlorine
Bromine
Iodine
Ozone
Arsine
Aniline
Phenol
Diethyl ether
Acrolein

(3) This group of gases and vapors requires special absorbers or sampling devices:

(a) Benzene, toluene, and xylene—absorb in nitrating acid in fritted-glass Petri tube at 0.25 liter per minute, or in glass-bead column at 0.05 liter per minute.
(b) Nitrogen dioxide—use several fritted bubblers in series, condense with liquid nitrogen or collect in sampling bottles.
(c) Nitric oxide and carbon monoxide—collect in sampling bottles or tubes.
(d) Halogenated hydrocarbons—pass through combustion apparatus and collect acid halides and free halogen in any suitable absorber, or absorb in amyl acetate using fritted bubblers.

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[44] *Am. Pub. Health Assoc. Yearbook 1939–40,* p. 92.

B. ADSORPTION

Adsorption is the phenomenon of the condensation on the surfaces of solids of a layer of a gas (or vapor), liquid, or solid which comes into contact with that solid. The factors that govern the amount of substance adsorbed are the area of the solid adsorbent, the pressure or concentration of the gas or vapor, the temperature of the system, and the characteristics of the adsorbing agent and the substance adsorbed. The theory of adsorption has been discussed by Langmuir.[45] More general text discussions are given by Getman and Daniels[46] and by Kraemer.[47]

The adsorbing properties of silica gel and other precipitated hydrous oxides and hydroxides, of charcoal, of dehydrated zeolites, and of many other porous and even nonporous materials have been studied. The principal adsorbing media used in industrial-hygiene chemistry, however, are activated charcoal and silica gel. Some impregnated porous materials also are used.

The efficiency of the various adsorbents varies widely among themselves and also for the materials adsorbed. One should note that even a good adsorbing agent will not adsorb everything even if its capacity is undiminished. Thus toxic smokes like diphenylaminechloroarsine will go right through the activated charcoal in a gas mask and also in an analytical determination. Special filtering must be used to trap such substances. Substances like phosgene, which hydrolyze readily, may not be adsorbed except on anhydrous activated charcoal.

1. *Activated Charcoal*

Activated charcoal, also known as decolorizing charcoal, is a type generally made from vegetable matter specially treated to render it highly adsorbent toward gases, vapors, and coloring matters. The U. S. P. product is in the form of a fine black powder, which is odorless and tasteless and contains 5–15 per cent of moisture and 2–3 per cent of ash. The form used for the adsorption of gases and vapors is generally composed of granules of 8–14 mesh. A very active form of charcoal is made from coconut shells, peach pits, and other shells and pits. Processes have been developed for the production of very highly activated charcoal from saw-dust, coal, and hardwood charcoal.[48] Large quantities of activated charcoal are used commercially for the recovery of solvent vapors, of gasoline from natural gas, of light oils from manufactured gas, for the removal of odors from air, the purification of carbon dioxide gas, etc.

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[45] I. Langmuir, *J. Am. Chem. Soc.*, *38*, 2267 (1916). *Ibid.*, *40*, 1361 (1918).

[46] F. H. Getman and F. Daniels, *Outlines of Theoretical Chemistry*, Wiley, New York, 1937.

[47] H. S. Taylor, *Treatise on Physical Chemistry*, Van Nostrand, New York, 1931.

2. *Silica Gel*

Silica gel is a precipitated silicic acid in the form of lustrous granules, specially prepared and adapted for the adsorption of various vapors. It can be used for the adsorption of water and can be regenerated when used for this purpose by heating in a stream of air at a temperature of 110–150° C. Where silica gel is used as the adsorbent, two tubes containing it are generally used because it is less efficient than activated charcoal. However, it has advantages in that its weight upon equilibration remains constant to a greater degree than activated charcoal.[49]

3. *Porous Materials*

Impregnated porous materials can be called absorbents as well as adsorbents, for the lines in these instances cannot be drawn sharply. Asbestos impregnated with sodium hydroxide is used for trapping carbon dioxide. Asbestos upon which has been precipitated silver oxide is used for the absorption of hydrogen sulfide. Other instances are the use of porous stones prepared with manganese dioxide from potassium permanganate precipitation for the adsorption of sulfur dioxide and the trapping of carbon disulfide on stone soaked in sodium ethylate.

4. *Adsorption Value*

The adsorption value of any material may be considered under two heads: (1) activity and (2) capacity.[49] Either may be tested by standard tube tests.

The adsorbent under test is filled into a sample tube of specified diameter, namely 2 cm., to a depth of 10 cm., by a standard method for filling tubes as described below; a standard concentration, usually 1,000 or 10,000 parts per million of a contaminant in air of a definite humidity, usually 50 per cent, is passed through the adsorbent at a rate of 500 ml. per square cm. per minute. The concentration of the entering contaminant in the air is determined by analysis. The length of time is noted from the instant the gas-air mixture is started through the adsorbent to the time the gas or other contaminant or some toxic or irritating reaction product of the gas begins to come through the adsorbent as determined by some qualitative test. Quantitative samples of the outflowing gas are then taken at known intervals and from the amount of gas found in the effluent sample, the per cent efficiency of the adsorbent at the corresponding time is calculated from the formula given on page 80.

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[48] A. B. Ray, *Ind. Eng. Chem., 32,* 1166 (1940).

[49] S. Moskowitz and W. J. Burke, *N. Y. State Ind. Bull. 17,* 168 (1938).

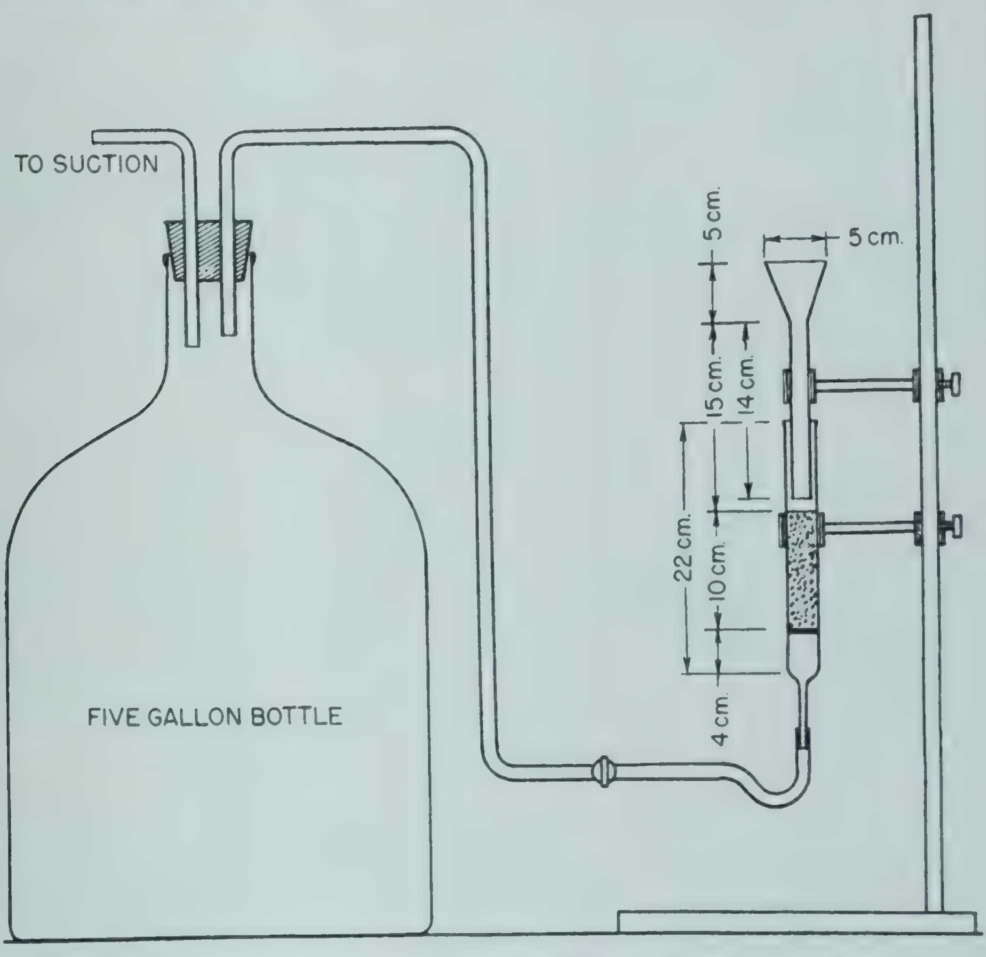

Fig. 46. Apparatus for filling absorption tubes (inside dimensions).

Standard Method of Filling Tubes.[50] The adsorption tube and funnel (Fig. 46) are supported in a vertical position with the funnel stem "centered" in the tube. The distance from the apex of the funnel to the upper layer of adsorbent when the adsorption tube is filled to the desired height should be 15 cm.

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[50] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem.* *11*, 519 (1919).

Pour the entire sample of adsorbent on a large sheet of rubberized fabric and mix thoroughly by rolling the sample. This may be done by lifting opposite corners of the fabric alternately. Smooth out the sample on the fabric and take portions with a spoon at regular intervals of space over the entire surface of the sample so as to insure having a representative portion for the test. Pour the adsorbent from the spoon, a few grains at a time, so that no grains have a free fall through the orifice of the funnel. The time for filling a 2.0-cm. tube to a height of 10 cm. should be not less than 1.5 minutes. The tube should not be tapped at any time. Connect the tube to a strong source of suction and draw air through it at least 5 times to remove dust. In removing dust from the adsorbent, the stopcock is turned on quickly for 1 or 2 seconds and quickly closed.

C. ABSORPTION

The choice of an absorbing agent is governed primarily by the ease with which the absorbed contaminant can be estimated. Another important factor is, of course, the efficiency with which the absorbent acts. Some mention of solid absorbents was made in a prior section of this chapter.

In the analysis of the gross components of air or of mine gas or fuels, such as natural gas and producer gas, there are only a few well-known components of these gas mixtures and for their absorption only a few absorbents are used. For complete details concerning the analysis of gas, the reader is referred to the bibliography at the end of Chapter XI.

The principal absorbing solutions used in the analysis of gross components of gas mixtures are sulfuric acid, potassium hydroxide, silver nitrate, pyrogallol, cuprous chloride, acid ferrous sulfate, nitric acid, and bromine.

In the analysis of industrial hazards the number of substances used as absorbents is very much greater. Each determination described in the text notes the absorbent to use and the concentration that will give a relatively high efficiency. Table 3 lists the device, absorbing reagent, and the efficiency of absorption for some of the gases and vapors commonly sampled. The rated efficiency of the devices mentioned in Table 3 has been questioned by some investigators.

TABLE 3

Gases Determined by Various Absorbing Devices[51]

Device	Air flow	Gas	Absorbing reagent	Efficiency[a]	Reference
Impinger	1 c.f.m.	Sulfur dioxide	NaOH	80–90% A	Paluch
		Sulfur dioxide	NaOH	Not checked	Gurney
		Sulfur dioxide	I_2	90% B	Barnes
		Acetic acid	NaOH	95% A	Elkins
		Ammonia	H_2SO_4	95% A	Paluch
		Ammonia	H_2SO_4	Not checked	Buxell
		Hydrochloric acid	Na_2CO_3	Not checked	Buxell
		Nitric acid	Na_2CO_3	Not checked	Buxell
		Chloronaphthalene	Amyl acetate	About 90% B	Elkins
		Ozone	KI	95% B	Barnes
		Nitrogen dioxide	KI	95% B	Barnes
		Nitrogen dioxide	NaOH	80% B	Elkins
		Nitrogen dioxide	NaOH	About 30% A	Elkins
		Nitrogen dioxide	Na_2CO_3	Not checked	Buxell
		Mercury	I_2	90% B	Barnes
		Hydrogen sulfide	I_2	50% A	Paluch
	½	Phenol	NaOH	90% A	Barnes
		Formaldehyde	NaOH	90% A	Barnes
	1	Hydrogen chloride	NaOH	80% A	Fehnel
Two impingers (in series)	1 c.f.m.	Hydrogen chloride	NaOH	ca 90% A	Fehnel
Single fritted bubbler	5 l.p.m.	Sulfur dioxide	NaOH	95% A	Paluch
		Hydrogen sulfide	I_2	95% A	Paluch
	4	Sulfur chloride	NaOH	95% A	Elkins
	10	Chloronaphthalene	Amyl acetate	90% B	Elkins
	2	Carbon disulfide	Alcoholic KOH	95% B	Elkins
	1	Carbon dioxide	Dilute $Ba(OH)_2$	60-80% B	Elkins
	1	Hydrochloric acid, chlorine	$NaAsO_2$	95% A	Fredrick
	1	Bromine	KOH	——	Deery
	1	Bromine	KI	95% B	Goldman
	1	Nitrogen dioxide	NaOH, H_2O_2	90% A	Coleman
	1	Nitrogen dioxide	H_2SO_4, H_2O_2	90% A	Coleman
	3-14	Hydrogen chloride	NaOH	ca 95% A	Fehnel
Two fritted bubblers (in series)	1 l.p.m.	Sulfur dioxide	I_2	——	Deery
	5	Hydrochloric acid	NaOH	95% B	Fredrick
	5	Phosgene	NaOH	95% B	Fredrick
	5	Nitrogen dioxide	NaOH	50-70% A	Fredrick
	5	Nitrogen dioxide	H_2SO_4, H_2O_2	50-70% A	Fredrick
	5	Nitrogen dioxide	Na_2O_2	50-70% A	Fredrick
Three fritted bubblers (in series)		Phosphine	KBr, Br_2	——	Burke
	0.5	Phosgene	Aniline solution	——	Burke
	0.5	Ether	H_2SO_4, $K_2Cr_2O_7$	——	Burke
Nichols absorber	1 c.f.m.	Sulfur dioxide	I_2	——	Fluck
		Chlorine	KI	95%	Fluck
Semi-fritted Petri tube	0.25 l.p.m.	Benzene	Nitrating acid	95% A	Elkins
Glass-bead column	0.05 l.p.m.	Benzene	Nitrating acid	95% A	Elkins
	1	Hydrochloric acid, chlorine	$NaAsO_2$	——	Gurney
	1	Hydrogen cyanide	Na_2CO_3	——	Gurney
Multiple absorber	1 l.p.m.	Carbon tetrachloride	Amyl acetate	90% A	Elkins
10-bulb Meyer tube	0.2 l.p.m.	Ozone	KI	95% A	Fredrick
Liquid-nitrogen trap	0.2 l.p.m.	Nitrogen dioxide	——	95% A	Fredrick

[a] "A" indicates determined on known concentration of substance.
"B" indicates calculated from amount found in second absorber.

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[51] *Am. Pub. Health Assoc. Yearbook 1939–40*, p. 98.

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CHAPTER V

The Chemical and Microscopic Estimation of Dust

Dust is the greatest single industrial hazard. More workmen are incapacitated for duty because of exposure to dust than for any other cause. This incapacitation results from the damage to which the respiratory tract in particular and the body in general are subjected by inhalation of dust. It was explained in Chapter I that silicosis is caused by the inhalation of dust which contains quartz. Silicosis is defined as a chronic disease of the lungs in which there is a marked increase of fibrous or scar tissue. Associated with diseases like silicosis and asbestosis, which result, respectively, from the inhalation of silica- and asbestos-bearing dusts, is the increased morbidity and mortality rate from the respiratory diseases like tuberculosis, pneumonia, chronic bronchitis, and pleurisy. The inhalation of metal-bearing dusts, such as lead dusts or fumes of manganese and other metals, causes general systemic poisoning of industrial workers. It is important to realize that the silica-bearing-dust hazard is not by any means limited to mining in or working with rock of high silica content or quarrying.

As an example of other industries in which this hazard exists we may take that of foundry workers. In a report[1] of a study on the dust hazard in foundries of New York State, it was found that 2.7 per cent of 12,000 workers had silicosis and that 4.5 per cent had fibrosis. Hatch[2] shows that in foundries this hazard is due to the dispersion of silica dust from the sand used in the molds and cores for metal castings. The steps of metal pouring, of shakeout (that is, the removal of castings from molds and the core from the casting), and of sand reconditioning for further use provide the opportunity, if not sufficiently guarded against, to disperse large quantities of silica-bearing dust.

Fairhall[3] lists as the most important inorganic dusts and fumes in addition to silica-bearing and asbestos-bearing dusts, those of arsenic, lead, phosphorus, manganese, zinc, sexavalent chromium compounds, fluorides, silicofluorides, and the basic salts of calcium and barium hydroxides. Among the more important organic chemical dusts he lists *p*-nitroaniline, dinitrobenzenes, chloronitrobenzenes, picric acid, nitronaphthaline, *p*-phenylenediamine, and tar dust.

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[1] *N. Y. State Ind. Bull. 17,* 61 (1938).

[2] T. Hatch, *N. Y. State Ind. Bull. 17,* 114 (1938).

[3] L. T. Fairhall, *J. Ind. Hyg. Toxicol., 18,* 669 (1936).

There can be no question that the diminution of the dust hazard in all trades will result in a corresponding diminution of morbidity and mortality from tuberculosis and other respiratory diseases.

A. DEFINITION OF DUSTS, FUMES, SMOKES, MISTS AND FOGS, AND VAPORS

Particles dispersed in the atmosphere both of the outside and of the workshop may be classified into a number of groups based on particle size, degree of dispersion, and whether they are accidentally present in the atmosphere because of some mechanical or chemical process of dispersion or whether they are normally present. The particles normally present in the atmosphere are due to the action of the winds, rain, tides, variations in weather, volcanoes, meteoric dust, and the decomposition of vegetable and animal matter. The particles accidentally present in the atmosphere are those which have come about through the development of civilization. Every fire, whether for the production of heat or of power, every grinding or rubbing action, and in general all mechanical-friction industrial and constructional activity creates dust. For the purposes of the study of industrial dusts and air pollution, atmospheric components, other than the normal gaseous components, can be classified as particulate and nonparticulate matter. The particulate matter consists of *dusts, fumes, smokes, mists, and fogs.* The nonparticulate matter consists of *vapors* and *gases.*

1. Dusts

Dusts may be defined as aerosols of a particular type, that is, they are disperse systems in which air is the continuous phase, or dispersion medium, and some solid material is the dispersed phase, or dispersoid. Dusts are sometimes called colloidal systems but such a definition is too strict, for in the main dusts are not true colloidal systems even though they are disperse systems. They settle out, whereas a true colloid will not settle.

Broadly speaking, atmospheric dusts are dispersions of solid materials in air. The particles of which they are composed vary in size from the submicroscopic to the visible. Drinker and Thomson[4] define dusts as particles or aggregates of particles, 150 microns [150 μ] to 1 micron [1 μ] in diameter, that are thrown into the air by mechanical agencies during the processes of grinding, crushing, blasting, drilling, and other industrial and constructional processes. One micron is equivalent to 1 μ, that is, one-thousandth of a millimeter [0.001 mm.]. Expressed in other units, one micron is equivalent to 1×10^{-4} cm., that is, one-ten thousandth of a centimeter, and to 10,000 Å, ten thousand Ångstrom units.

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[4] P. Drinker and R. M. Thomson, *J. Ind. Hyg.*, 7, 261 (1925).

For the industrial-hazard aspect, dusts may be considered as particles or aggregates of particles suspended in the atmosphere, of some size that is capable of being inhaled.[5] This restricts the particle size to the range of 0.5 to 10 μ.

Harrington[6] points out, however, that asbestos fibers 200 μ in length have been found in the lungs of men and must have had a detrimental effect. It is probable that dust particles even of larger size do have harmful effects in that they clog the air passages leading to the lungs, which might ordinarily trap more harmful particles thus permitted to pass into the lungs.

De Mello[7] gives an even broader definition of dust as a generic name for all solid particles of any size, nature, or origin, suspended or capable of being suspended in the air.

The particle size of true colloidal systems is arbitrarily set as that of particles having diameters between 0.001 and 1 μ. Those disperse systems having particles smaller in size are generally considered true solutions and those having particle sizes larger than 1 μ are generally considered ordinary matter. Thus we see that only in the lower limits of particle size do dusts fall within the definition of colloidal systems.

2. *Fumes*

Fumes are colloidal systems which are formed from chemical reactions or by processes like combustion, distillation, sublimation, calcination, and condensation. The particle size varies from 0.2 to 1 μ. Examples of fumes are the disperse systems formed from burning zinc or magnesium with the formation of zinc and magnesium oxides; the formation in air of ammonium chloride from the reaction of ammonia and hydrogen chloride; the reaction and condensation of water with titanium tetrachloride and burning phosphorus.

[5] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1938).

[6] D. Harrington, *U. S. Bur. Mines, Inform. Circ. 7072* (1939).

[7] J. B. de Mello, *J. Ind. Hyg. Toxicol., 28,* 162 (1946).

3. *Smokes*

Smokes are complex colloidal systems that are generally formed by the incomplete combustion of carbonaceous and other material. Particles of a smoke are generally less than 0.3 to 0.5 μ in diameter. Drinker and Hatch[8] use the word with particular reference to the disperse systems that are organic in origin, such as the smoke from burning tobacco, wood, oil, coal, etc. Necessarily, as is clear from the chemical-warfare point of view, a prerequisite of smoke is that it have a definite degree of optical density.

4. *Mists and Fogs*

Mists and fogs are disperse systems in which the particle size varies greatly. They are akin to fumes rather than to smokes. They carry the implication of a liquid rather than that of a solid dispersed in the atmosphere. They are generally formed by the condensation of water vapor on nuclei such as submicroscopic particles of dust or gaseous ions, or by the atomization of liquids.

5. *Vapors*

Vapors are gaseous bodies which are formed from liquids by increase of temperature but which readily resume their fluid form because of decrease in temperature.[9] Obviously, as true vapors they form true solutions with the atmosphere. Our interest in them lies in the fact that while they do form true solutions with air in their vapor state, as soon as they regain their liquid state they form mists, fogs and fumes.

B. CLASSIFICATION AND PHYSIOLOGICAL ACTION OF DUSTS

It is possible, as has been explained, to classify dusts according to particle size and according to origin, and to place them in two main groups according to physiological action, namely, those which cause respiratory disorders and those which cause systemic poisoning. It is of value, however, to classify dusts with respect to physiological action on a broader basis. Thus Oliver[10,11] divides dusts into those which have a mechanical and irritant action, and those of the chemical and toxic, or caustic, types.

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[8] P. Drinker and T. Hatch, *Industrial Dust*, McGraw-Hill, New York, 1936.

[9] F. Flury and F. Zernik, *Schaedliche Gase*, Springer, Berlin, 1931.

[10] R. W. Goldberg, *Occupational Diseases*, Columbia Univ. Press, New York, 1931

[11] T. Oliver, *Diseases of Occupation*, Dutton, New York, 1916.

Thompson[12] divides the physiological action of dust on human beings into four types:

(1) Mechanical obstruction of air passages
(2) Laceration of mucous membranes
(3) Conveyance of toxic material into the system
(4) Conveyance of germs into the system

Actually dusts cannot be placed into groups which show a specific type of physiological action because no dust is composed of a single variety of material.

The physiological response to dusts is grouped as follows by Drinker[13]:

(1) Specific lung diseases such as silicosis and asbestosis.

(2) Toxic systemic effects caused, for example, by breathing of such toxic dusts as lead, cadmium, and radium.

(3) Metal-fume fever, which follows the inhalation of finely divided particles such as zinc oxide.

(4) Allergic manifestations that result from breathing dusts such as pollen and certain types of pulverized wood and flour.

The physical, chemical, and physiological actions of dusts may also be grouped as in the following classification[14]:

(1) Cutting dusts—these are in the main composed of minute crystalline or amorphous particles which have sharp cutting edges such as sand, stone, lime, steel, asbestos, glass, minerals, etc.

(2) Irritant dusts—this group is composed of vegetable and animal matter such as wood, ivory, hair, and fibers such as wool, silk, cotton,[15] flax, hemp, and the fabrics and cordage made from them.

(3) Inorganic poisons and compounds of mercury, copper, arsenic, lead and even soluble compounds such as the sulfates of iron, copper, and sodium.

(4) Organic poisons such as tobacco and, in general, organic compounds and drugs.

(5) Obstructive and irritating dusts such as soot, coal, flour, and starch.

It is readily seen that this classification also falls into the grouping of physical action (mechanical and irritating), namely (1), (2), and (5), and chemical action, (3) and (4). It must be borne in mind, however, that dusts act both physically and chemically in some measure on the body.

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[12] W. G. Thompson, *Occupational Diseases,* Appleton, New York, 1914.

[13] P. Drinker, *J. Ind. Hyg. Toxicol., 18,* 524 (1936).

[14] *N. Y. State Special Bull. 90* (1918).

[15] B. H. Caminita, W. F. Baum, P. A. Neal, R. Schneiter, *U. S. Pub. Health Service, Bull. 297* (1947).

A more comprehensive classification of dusts according to physical, chemical, and physiological effects is that of Sayers.[16]

A. Organic dusts

Organic dusts are those which contain carbon, and are originally supposed to have come from organized substances derived from animal or plant life. Thousands of organic substances are made synthetically by chemical processes, such as dyestuffs, explosives, drugs, and similar substances.

(1) Nonliving organic dusts
  (a) Toxic and/or irritant dusts—all organic dusts which produce untoward symptoms, either systemic or local. Those producing local symptoms are usually described as irritant; those producing general or systemic symptoms are termed toxic. A dust may be both toxic and irritant. Among the chief offenders are *p*-nitraniline, the dinitrobenzenes, the chlorodinitrobenzenes, picric acid, nitronaphthalene, *p*-phenylenediamine, and trinitrotoluene. Many organic substances and dusts cause dermatitis.
  (b) Allergic dusts—many apparently innocuous substances may produce reactions in persons of peculiar personal susceptibility. The term allergy is used to describe this condition of hypersensitiveness, or susceptibility, and allergic phenomena most frequently manifest themselves in skin reactions. They may cause acute reactions elsewhere in the body; thus when the respiratory tract is involved, diseases such as hay fever or asthma may result. Substance like pollens from plants, horsehair, furs, feathers, and the like may cause these illnesses. Some persons are also allergic to hexamethylenetetramine and formaldehyde. Impregnated woods from abroad may also cause illness.

(2) Living organic dusts
  (a) Bacteria—most important is anthrax bacillus. Other illnesses traced to infected dusts are tetanus, diphtheria, tuberculosis, smallpox, typhoid, and others.
  (b) Fungi[17]—dusts containing the mycelia and spores of parasitic fungi give rise to annoyance and discomfort.

B. Inorganic dusts

(1) Toxic and/or irritant dusts—toxic dusts are those which are inherently toxic when inhaled, ingested, or otherwise absorbed. Among those which produce systemic poisoning, some of which are also irritant, are the dusts from heavy metals and their salts, such as lead, mercury, arsenic, cadmium, zinc, and similar metals. Irritant dusts are injurious by reason of their strong irritative or corrosive properties. As a rule, inhaled irritant substances immediately cause a reaction in the upper respiratory tract of such severity that they are pre-

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[16] R. R. Sayers, *U. S. Public Health Repts., 53,* 217 (1938).
[17] A. R. Smith, *N. Y. State Ind. Bull., 18,* 15 (1939).

vented from reaching the lungs, although they may cause lung damage by extension of inflammation if the mucous membrane is corroded. Lime, calcium oxide, and the dichromates are examples of irritant dusts. An inorganic dust may possess both toxic and irritant properties, and the poisoning produced may be the combined effect of more than one mode of entrance into the body. Lead oxide, carbonate, and chromate are the most widely prevalent directly poisonous dusts. Alkalies and metallic oxides are common causes of dermatoses.

(2) Fibrosis-producing dusts—the most important are the inorganic, slightly soluble dusts which cause fibrous changes in the lung tissues, some of which are serious and some of which cause little or no disability. So far as is known, no inorganic substances other than silicon derivatives cause more than a very moderate degree of fibrosis of the lung. Examples of siliceous dusts are granite, quartz, sand, pumice, slate, and similar substances. Asbestos causes an allied disease.

(3) Non-fibrosis-producing dusts—these are inert, *i.e.*, they do not cause fibrous tissue to be produced. Included among them are alundum, coal, corundum, emery, limestone, magnesite, marble, plaster of Paris, gypsum, and polisher's rouge.

Characteristics of Dust

There are three important characteristics of dust that control its action as an industrial hazard. They are:

(1) Particle size and frequency
(2) Quantity
(3) Chemical action

It is known that particle size and frequency of distribution play an important part because it has been shown that in normal atmospheres, 97 per cent of outdoor dust particles are less than 1 μ in diameter. Practically no dust particles larger than 1.5 μ are to be found in uncontaminated outside air. On the other hand, practically all dust particles in an industrial establishment are larger than 1 μ. Table 6 and Figure 72 show the difference between the size frequency of outdoor dust and industrial dust. About 60 per cent of the particles have a diameter between 1 and 3 μ.

It has been shown that silicosis develops more rapidly the more intensive the exposure to dust. Thus we need methods to determine the amount of dust in the air of an industrial establishment. Insofar as the chemical composition of dusts is concerned, they will be treated as air contaminants in the subsequent chapters of the book. This chapter will concern itself with the methods for the determination of the quantity of dust and the estimation of particle size and frequency.

C. DUST-SAMPLING APPARATUS AND METHODS OF SAMPLING

There are a number of methods and apparatuses used for the sampling of dust by means of which the aforementioned determinations can be made. These methods enable us to estimate the quantity of dust by (1) counting of dew drops which have condensed around particles of dust, (2) weighing the particles, (3) estimation of the intensity of some physical property, generally photometric methods, (4) rapid centrifugal methods, (5) electrostatic methods, and (6) counting the number of particles after impingement or absorption. Each of these methods has advantages and disadvantages. The more important will be described.

The methods used to sample dusts so that the aforementioned means of estimation can be used fall into groups classified according to the physical principle utilized by the sampling instrument.[18] The more important methods used for sampling dust of both indoor and outdoor atmospheres are condensation, sedimentation and deposition, absorption, electrostatic flocculation, thermal flocculation, filtration, and impingement. These methods are by no means mutually self-exclusive, as many instruments use more than one physical principle.

Dust studies concerning air pollution may be made with the same instruments as are used for indoor dust determinations but some devices and methods have been particularly developed for outdoor dust determinations.

1. Aitken Nuclei Counter

As early as 1890, Aitken[19] devised an apparatus making use of the fact noticed by Coulier[20] in 1875, that dust in air could be rendered visible by reducing the pressure within a containing vessel, causing the moisture present in the air to condense on the dust particles. Since that time, Aitken[21] and others have modified his original apparatus. The new forms still depend for their operation upon the facts that when air containing condensation nuclei becomes saturated by having its pressure suddenly reduced, a condensation of water vapor takes place upon the nuclei, and the droplets formed by this condensation settle rapidly. By means of a simple microscope, built into the instrument, the number that settle on a glass plate is easily read. From this number and the dimensions of the instrument the number of condensation nuclei in a cubic centimeter of air can be calculated.[22]

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[18] L. Greenburg, *U. S. Pub. Health Repts., 40,* 765 (1925).

[19] J. Aitken, *Proc. Roy. Soc., 18,* 39 (1890–1).

[20] M. Coulier, *J. Pharm., 22,* 165 (1875).

[21] J. Aitken, *Collected Scientific Papers,* Cambridge, 1923.

The instrument consists of an air chamber, the walls of which are covered with moistened blotting paper, a calibrated pump for the taking in, or expulsion, of a given volume of air, or for the sudden expansion of this air, a glass plate ruled in millimeter squares, a simple microscope with dark-field illumination, and the necessary stopcocks for taking in or expelling air from the chamber. The air chamber is 1 cm. deep and has a capacity of about 7 ml. The total capacity of the pump is about one-fifth of that of the air chamber. When determining the number of nuclei in a given sample of air, the expansion of the air in the chamber should be repeated from 2 to 10 times, until no droplets are formed in the chamber upon successive expansions. The sum of all the droplets formed on successive expansions is taken as the number of condensation nuclei present in the air.

The number of condensation nuclei present in the air is much greater than that of the dust particles. Ives[22] and his co-workers found that the average number of dust particles present in a ml. of air in the winter time was 815, whereas the average number of condensation nuclei in a ml. of air was 207,000. Condensation nuclei may be solid, liquid, or even gaseous particles such as gaseous ions, upon which water vapor condenses when the air becomes saturated or approaches saturation.

It is evident then that insofar as actual dust determinations are concerned, the Aitken instrument and its modifications are inadequate, for condensation occurs not only on dust particles but also on other condensation nuclei such as large molecular aggregates and gaseous ions. On the other hand, no instrument will give information as to the number of condensation nuclei in an atmosphere as will the Aitken counter.

2. *Sedimentation and Deposition Methods*

Sedimentation methods of dust sampling are of little value as a means of measuring the number of dust particles that a sample of air contains, unless special devices such as the Green[23] cell are used. On the other hand, sedimentation methods are extremely useful for collecting samples of settled dust.

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[22] J. E. Ives, R. H. Britten, D. W. Armstrong, W. A. Gill, and F. H. Goldman, *U. S. Pub. Health Service, Bull. 224* (1936).

[23] H. L. Green, *J. Ind. Hyg., 16,* 29 (1934).

The dust caught on a plate by sedimentation is some function of the dust in the air but the exact mathematical relationship is not known. Green[23] uses a cell of known capacity provided with a rapid means of closing so that the air under examination can be sampled quickly. There is a $^1/_2$-inch cover slip on the bottom plate, upon which the dust in the cell settles. The cell is moved through the air until it is purged. The ends are closed quickly and the cell is placed in a vertical position for 3 hours to permit the dust to settle. Temperature and vibration must be controlled.

Labyrinth. Cylindrical or other shape labyrinth dust collectors are devices used for collecting larger samples of dust over longer periods of time. This period may extend from 1 to 8 weeks. The purpose of the long sampling time is to obtain sufficient samples of dust to make a complete analysis. The device described by Matthews[24] consists of 32 copper plates held together by a long brass tube and kept in place at right angles by short equal lengths of brass tube. The baffle assembly is wrapped with an overlapping sheet of celluloid, held in place by a spiral winding of woolen yarn. Then the entire assembly is placed in a copper casing. The dusty air is drawn through by suction and the dust deposits on the plates of the baffle arrangement. Particles of a size larger than a given diameter may be excluded by means of an elutriator.

The efficiency of the labyrinth varies with the rate of flow and the type of dust. Most of the sample is collected in the first few sections of the labyrinth. The chief advantage of the labyrinth is that it enables one to obtain a large sample of uncontaminated dust that requires no further treatment. A further advantage is that the labyrinth sample is graded in particle size according to the different sections. The particle size falls off, so that in the last sections all the particles are 5 μ and under. These are the particles considered to be most dangerous to the lungs. The efficiency of the labyrinth is high for a dust like flint and low for a dust like asbestos.

Collection of Outdoor Dust. Ives[25] and his co-workers used the apparatus illustrated in Figure 47 for obtaining a sedimentation sample of outdoor dust. The apparatus consists of a large glass funnel 30 cm. in diameter, connected by a Pyrex glass tube, 4 feet 7 inches long, with a Pyrex glass 9-liter bottle. The funnel should be supported by a wooden framework so that its top is about 4 feet above the level of the roof where the air is being sampled. The tube connecting the funnel and the bottle passes through a hole in the roof and empties into the bottle, which is kept indoors underneath the roof so that any water that enters it will not freeze in the winter. The glass tubing also passes through a hole in a small fiber board over the mouth of the collecting bottle so that all other dust except that falling in through the tube will be excluded. The dust and rain, if any, may be allowed to accumulate on the funnel or in the bottle for a given period, say one week, and at the end of the given period, the funnel and tubing is washed down with

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[24] J. W. Matthews, *Analyst, 63,* 467 (1938).

[25] J. E. Ives, R. H. Britten, D. W. Armstrong, W. A. Gill, and F. H. Goldman, *U. S. Pub. Health Service, Bull. 224* (1936).

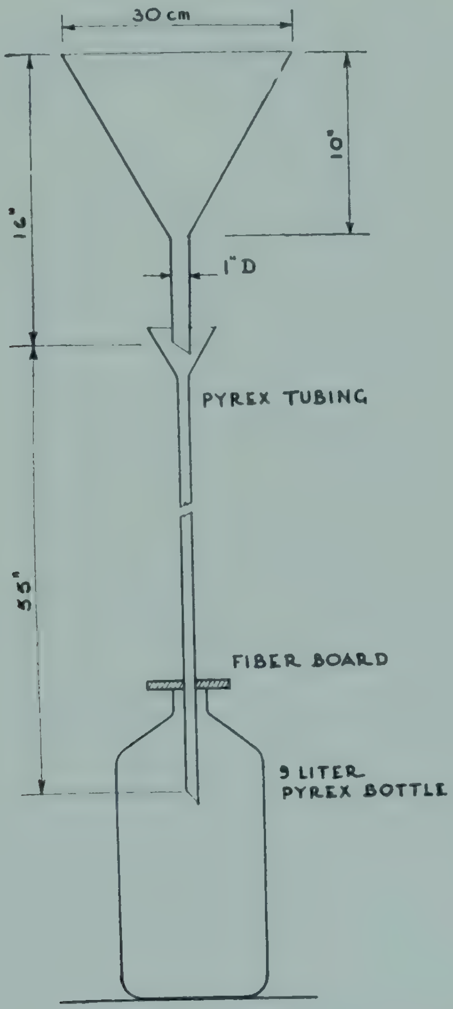

Fig. 47. Apparatus for collection of settled dust.

distilled water. The bottle may then be sealed and the contents analyzed in a laboratory.

The sootfall gauge used in the sootfall survey[26] of New York City in 1936 was a tin-lined copper can, 5 inches in diameter and 8 inches high, placed outdoors on a roof, as illustrated in Figure 48, by fastening it with wire to a 4-foot high wooden stand having a weighted base. In later surveys, the metal cans were replaced by wide-mouth gallon jars, $4^1/_4$ to $4^1/_2$ inches in diameter and about 8 inches high. Water to a depth of 3 inches was added to each gauge, but in cold weather Cellosolve was used in place of water to avoid freezing.

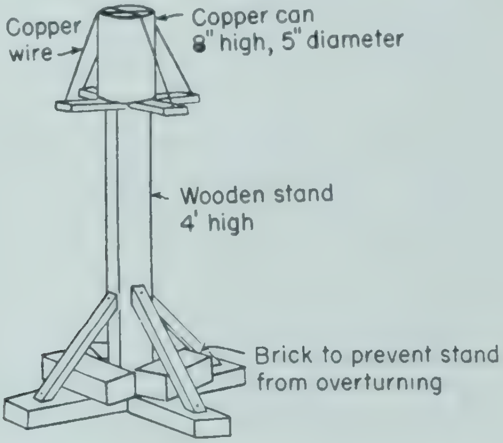
Copper wire
Copper can 8" high, 5" diameter
Wooden stand 4' high
Brick to prevent stand from overturning

Fig. 48. Gauge for the collection of settled atmospheric matter.[26]

At the beginning of each month the jars were replaced by other jars or the cans were emptied into sample jars, which were brought to the laboratory for analysis.

Procedure. Remove extraneous material such as leaves, twigs, paper, and the like, which cannot be considered as sootfall components, with the aid of a 20-mesh sieve. Filter the contents of each jar through a tared alundum crucible or a tared Gooch crucible equipped with a light asbestos pad to separate the insoluble from the soluble solids. Reserve the filtrate. Dry the crucible, cool, and weigh to obtain the weight of insoluble solids. Place the crucible in a Soxhlet extractor and extract the tarry material with carbon disulfide. Dry, cool, and reweigh. The difference in weight is considered to be tar. Char, heat the crucible in a muffle at 760° C. (1400° F.), cool, and weigh. The weight of the residue is the weight of ash. The weight lost on combustion may be considered carbon.

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[26] J. Siegel and B. Feiner, *Heating, Piping, Air Conditioning*, 17, 495 (1945).

The filtrate may be used for determinations of soluble solids, ash, ammonia, chlorides, and sulfates. Evaporate an aliquot portion in a tared, flat dish to estimate the total soluble solids. Dry, cool, and weigh. Ignite, cool, and weigh to determine the ash content. Estimate ammonia by steam distillation using an aliquot portion in a Kjeldahl flask and trapping the distillate in boric acid solution. Titrate the ammonia directly with standard hydrochloric acid. Determine the chloride by the Volhard method see (page 380) and sulfates by precipitation as barium sulfate (see page 311).

3. *Absorption Methods*

Absorption methods of dust collection consist, in general, of passing a known amount of air through some absorber in such a manner that the air will bubble through the absorbing medium, usually water. The water will wet the dust and bring it into suspension and the dust-free air will then pass through. Many of these apparatuses have been devised, for a fair estimate of both weight and count of dust can be obtained with them.

a. Palmer Device

One of these devices is that of Palmer.[27] This apparatus consists of a pear-shaped glass bulb at the base of which is a U-tube water trap. Air is drawn through the trap in such a manner that the water it contains is thrown up into the pear-shaped bulb section in the form of a spray. This spray is again trapped by an S-shaped exit tube. The spray washes the dust from the incoming air stream.

These absorption or washing methods, as they are termed by Greenburg,[28] have the pronounced drawbacks, first, that absorption may be far from complete and second, that many particles, particularly those of small diameter, may not be wetted and therefore will pass out unabsorbed. The use of the Palmer device has been replaced by impingement instruments also using the absorption principle. It is the opinion of the author that the use of wetting agents, that is,

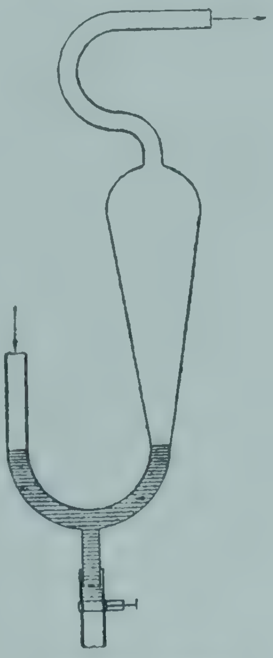

Fig. 49. Palmer Apparatus.

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[27] G. T. Palmer, *Am. J. Pub. Health, 6,* 54 (1916).

[28] L. Greenburg, *U. S. Pub. Health Repts., 40,* 765 (1925).

surface-active agents[29-32] or surface-tension depressants,[33] would greatly increase the efficiency of devices using the absorption principle.

b. Rapid Method

Most absorption methods use water as the absorbing medium, an aliquot portion of which is then evaporated in a tared dish, dried, and weighed, or the dust particles of which are counted microscopically. Naeslund[34] uses a different absorbing medium. He has developed a rapid method using olive oil.

With the aid of a water driven pump, or other suitable suction pump such as the vacuum pump of a vacuum tank of an auto or of a vacuum cleaner, aspirate air through a glass tube down into the bottom of a suitable shape such as a small absorbing test tube. Fill the tube half or two-thirds full with glass pellets, 3 to 4 mm. in diameter, and place on top of these a number of larger pellets to keep the small ones from being lifted by the passing air. Coat the tube, together with the glass pellets, with a thin layer of olive oil by pouring the oil into the tube containing the pellets so that all of the pellets are oiled. Drain off the excess oil by turning the tube upside down for a while on filter paper. Aspirate air at a comparatively high speed of 3 to 5 cubic meters per hour. The actual flow should be measured with a gas flowmeter of some type. From 10 to 30 cubic meters of air should be tested in streets and living quarters. One to 10 cubic meters are sufficient in dusty factories and work shops.

After the sampling is finished, fill the test tube with ether and shake. Remove the suction lead tube and pour the ether and pellets into a small funnel with an uneven piece of broken glass (as shown in Fig. 50) or some other device to keep the pellets but not the dust from passing through. Catch the ether in a centrifuge tube to the bottom of which is attached a thick walled capillary tube 1 mm. inside diameter and 2 cm. or more in length. Wash the tube, pellets, and funnel 4 or 5 times more with small portions of ether. Centrifuge and if necessary use a wooden pin to press down the dust so there will be an even line of demarcation. As a contrast use 2 or 3 mg. of red lead as the bottom layer (as explained on page 123). Read, if necessary, with the aid of a magnifying glass. Compare the height of the column obtained with known quantities of known dust.

This rapid method cannot give any estimate of the count of dust

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[29] *Ind. Eng. Chem.*, *31*, 66 (1939).

[30] T. Fuwa and G. A. Shattuck, *Ind. Eng. Chem.*, *15*, 230 (1923).

[31] H. L. Cupples, "Proprietary Surface Active Agents," *U. S. Dept. Agr., Agr. Research Admin., Bur. Entomol. Plant Quarantine* (1943).

[32] Morris B. Jacobs, *Synthetic Food Adjuncts*, Van Nostrand, New York, 1947.

[33] M. D. Thomas, *Ind. Eng. Chem., Anal. Ed.*, *5*, 193 (1933).

[34] C. Naeslund, *J. Ind. Hyg.*, *14*, 113 (1932).

particles. However, where a rapid method is desired to give some measure of total dust in an atmosphere, it will serve. It has the advantage that it does trap most of the dust and that the reagents used, namely, olive oil and ether, can be prepared practically dust free.

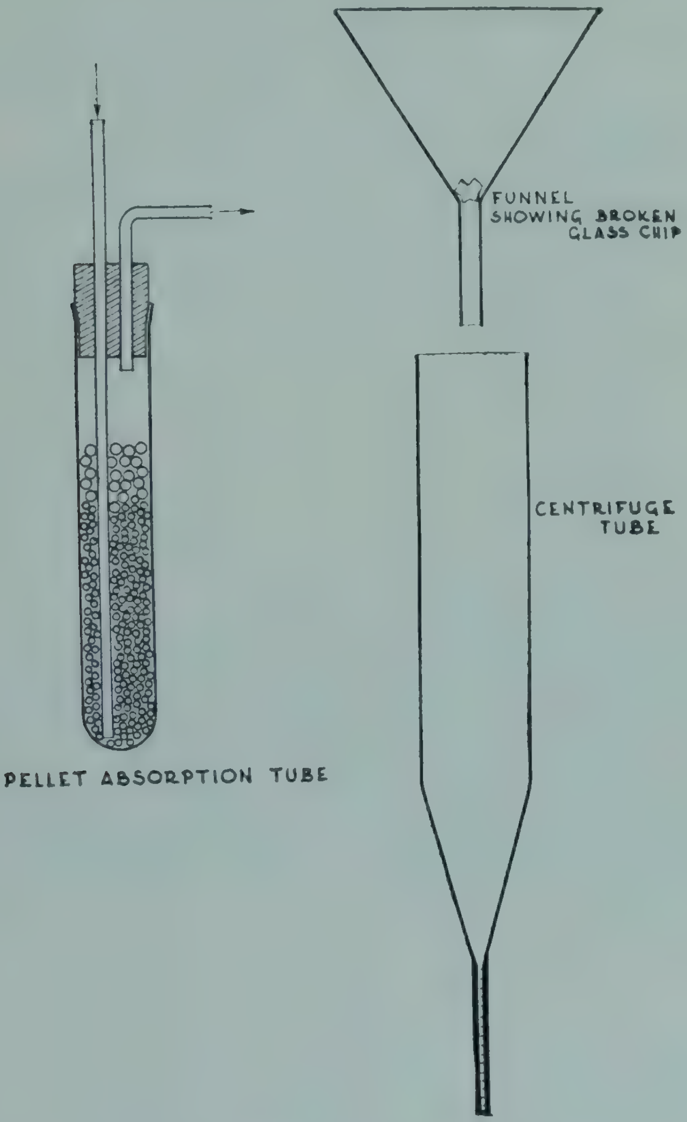
FUNNEL
SHOWING BROKEN
GLASS CHIP
CENTRIFUGE
TUBE
PELLET ABSORPTION TUBE

Fig. 50. Dust centrifuge tube and sampling apparatus.

4. Electrostatic Flocculation

Dust particles in the air can be caused to flocculate and thus precipitate by means of a high electric potential. The flocculation and precipitation are caused by (1) electrostatic attraction and (2) ionic bombardment of the electric wind created by the corona discharge.[35] The second cause is greater. Devices using the principle of electrostatic flocculation for dust sampling are commercially available.

Drinker[36] describes a comparatively simple apparatus that can be made from easily obtainable equipment. The larger model consists of a tube in which is centered a gold-plated drill-steel wire, which serves as one electrode. In the small apparatus, gold or platinum wire serves as one electrode. The other, outer electrode is made of either metal netting, of metal foil, or of copper wire wrapped spirally along the tube. Such wrappings must be pulled tight by hand and may be kept in place by friction tape. Celluloid foil or filter paper placed inside the tube is used as the collecting medium. The precipitating electrode must be kept well up the tube to insure efficient collection on the celluloid foil or filter paper. The observance of this precaution precludes dust from being caught on the glass tube itself.

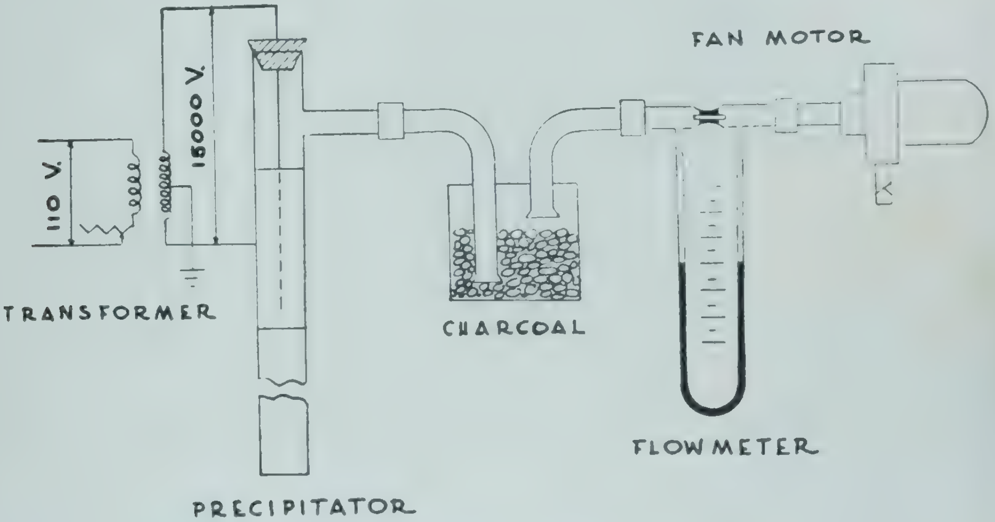

Fig. 51. Electrical-precipitator assembly.[29]

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[35] P. Drinker and T. Hatch, *Industrial Dust*, McGraw-Hill, New York, 1936

[36] P. Drinker, *J. Ind. Hyg.*, *14*, 364 (1932).

In operation, a sufficient volume of air, measured with a flowmeter, drawn by means of a compressed-air ejector or hand-size vacuum cleaner fan, is passed through the precipitating tube at about 50 liters per minute until a visible deposit of dust is obtained. The foil or filter paper containing the dust deposit is then removed from the tube and placed in a receptacle for transmittal to the laboratory.

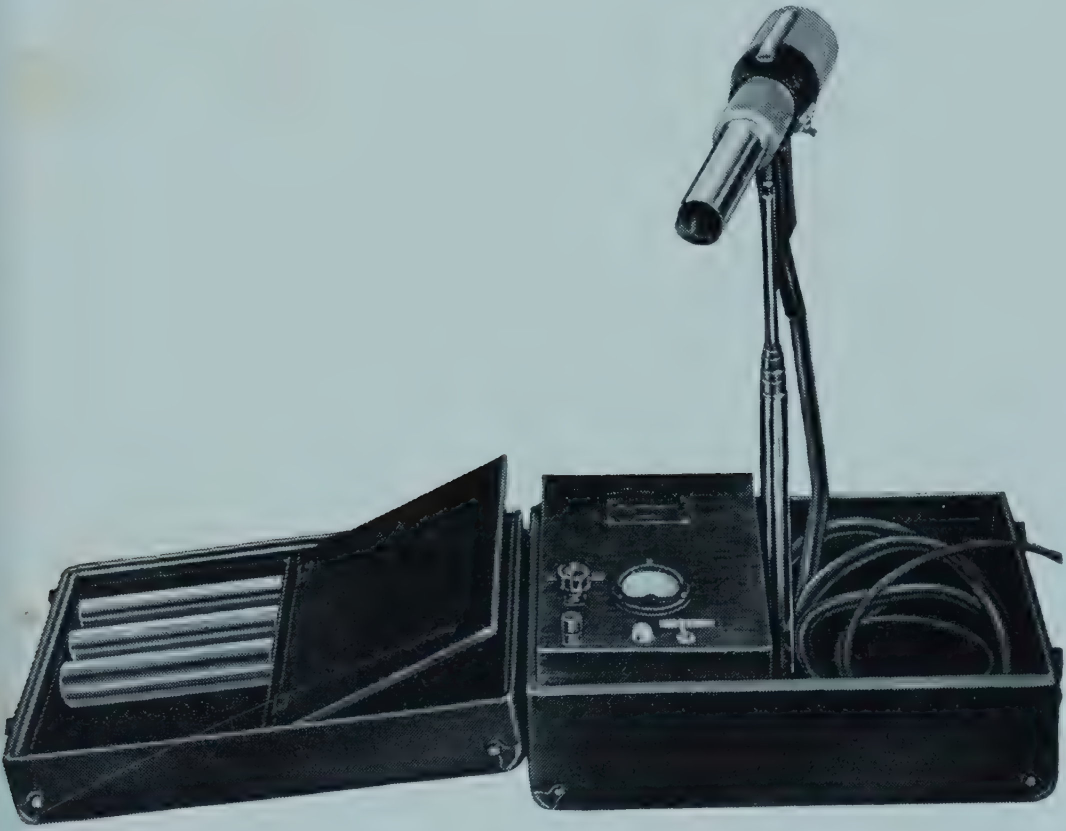

Fig. 51A. Electrostatic dust and fume sampler, including sampling tube kit. (*Courtesy Mine Safety Appliances Co.*)

Since gases of a toxic nature may be produced in the operation of this type of precipitating device, and because these gases react with the rubber stoppers and tubing of the apparatus, it is necessary to insert an absorbing vessel containing activated charcoal in the setup to absorb the noxious gases formed.

Electrolytic flocculation is used particularly well in the precipitation of smokes and fumes. It is not used so much for dusts because there are simpler apparatuses operating on different principles with an equal efficiency for dusts. The greatest disadvantages of the electrostatic precipitator is that it needs electric power, which is not always available, that noxious gases may be formed and must therefore be guarded against, and that the equipment is fairly complicated.

An electrostatic dust-weight sampler is described by Barnes and Penney.[37,38] A sample of dusty air is trapped in a cylinder and deposited electrostatically over its inside surface. A microscope slide placed in one side of the cylinder receives its proportionate share of the total dust, the dust particles being, in general, uniformly distributed over the slide. This slide can be removed, covered with a rectangular cover slip, and examined microscopically. Lea[39] has described a portable electrostatic precipitator.

5. *Thermal Flocculation*

Aitken[40] showed that smoke could be removed quantitatively from air by passing the air through a hot-cold tube. The smoke precipitated on the cold surface. This principle is used by Green and Watson.[41,42] Dusty air is drawn through a slot across which is a nichrome wire kept at 100° C. The walls of the slot are formed by cover slips, which are backed by brass blocks. The brass conducts the heat away and thus maintains a temperature gradient between the wire and the cover glasses. The dust deposits on the cover glasses and may be estimated.

6. *Filtration*

There are many methods using the principle of filtration as a means of collecting dust and fume samples. Many depend upon sucking the dust or fume through a weighed insoluble material such as filter paper, absorbent cotton, filter bags, cotton cloths, Gooch crucible with an asbestos mat, paper thimble, alundum thimble, etc. The dust or fume is then estimated gravimetrically with these media or the depth of a stain is compared. Others depend on filtration of the atmosphere to be tested through a soluble material such as sugar, salicylic acid, naphthalene, anthracene, etc., which is subsequently dissolved in water, alcohol, ether, or other appropriate dust-free solvent or is sublimed and the dust is

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[37] E. C. Barnes, *Am. J. Pub. Health, 26,* 274 (1936).

[38] E. C. Barnes and G. W. Penney, *J. Ind. Hyg. Toxicol., 20,* 259 (1938).

[39] W. L. Lea, *J. Ind. Hyg. Toxicol., 25,* 152 (1943).

[40] J. Aitken, *Collected Scientific Papers,* Cambridge, 1923.

[41] H. L. Green and H. H. Watson, *Med. Council Privy Council, Special Reprint 199,* London (1935).

[42] H. H. Watson, *J. Chem. Met. Mining Soc. S. Africa, 37,* 166 (1936); *Analyst, 62,* 232 (1937).

then estimated either by counting or refiltering through a tared device and subsequently weighing the collected dust. Among the more important of the first group are the Owens[43] automatic air filter, which is used to study outdoor atmospheric pollution; the koniogravimeter, a device used in Russia; the paper thimble; the Brown filter-paper method; the Silverman filter-paper method; and the bag test. The most important of the second group is the sugar-tube method. Filtering methods are among the most efficient for the collection and sampling of fumes.

a. Owens Automatic Air Filter for Estimating Air Pollution

The Owens automatic air filter[44] is a device for making a continuous automatic record of the pollution in the air. In this instrument a known volume of air is filtered through the outer portion of a disk of white filter paper, 7 inches in diameter, and the impurity present in the air is measured by the depth of shade produced on the filter paper. Two liters of air are filtered, at regular intervals of time, through a round spot $^1/_8$ inch in diameter. The filtering through each spot takes approximately 4 minutes, and from four to six spots are recorded in an hour. The disk is rotated by clockwork and makes a complete revolution in 24 hours. Since the instrument is in operation continuously during any period, a record of the variation in pollution is obtainable for that period. The degree of pollution, represented by the grayness of a spot, is determined by comparing its grayness with that of a standard scale of shades.

The standard scale of shades consists of a row of ten rectangles each $^1/_2$ inch square, varying in grayness from a very light gray, marked "1," to a very dark gray, marked "20." The ten shades are numbered 1, 2, 3, 4, 6, 8, 10, 12, 15, and 20, respectively. They are made by applying a standard wash of lampblack to white paper as many times as the number of the shade. The density of each shade is therefore a multiple of unit shade. Each shade has a hole $^1/_8$ inch in diameter punched in its center, and a spot on the disk is compared with a standard shade by inserting it under the hole. In comparing spots on the disk with the standard shades, it is sometimes difficult to obtain an exact match. Ives and his co-workers used the number that most nearly matched the sample spot, for example, calling a shade lying between 0 and 0.5, 0.

The Owens automatic air filter measures air pollution by the degree of blackness of a stain. Where the air pollution is caused by dust which is not black, the method fails unless different standards are prepared.

b. Koniogravimeter

The koniogravimeter,[45] a device used in Russia, designed to be worn by a workman, if desired, consists of a special set of tubes. These tubes are so arranged that they may be loaded with a filtering tube which can subsequently be dried and weighed. They are adjusted to nosepieces so that they can be worn by a worker as he performs his duties or by an investigator where the sampling of dust is to be done. They can also be attached to a vacuum pump. The gain in weight shown by the tared filtering tube shows the amount of dust inhaled by a workman in a given time.

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[43] N. Shaw and J. S. Owens, *The Smoke Problem of Great Cities,* Constable, London, 1925.

[44] J. E. Ives, R. H. Britten, D. W. Armstrong, W. A. Gill, and F. H. Goldman, *U. S. Pub. Health Service, Bull. 224* (1936).

[45] A. I. Burstein, *J. Ind. Hyg., 10,* 279 (1928); *12,* 24 (1930).

c. Paper Thimble

A standardized method of using the paper thimble for the sampling of dust is the method of Trostel and Frevert.[46] These investigators used Whatman extraction thimbles, 33 by 94 mm., containing a small amount of cotton wool (125 mg.), well fluffed out, for the purpose of supporting the dust and to prevent the clogging of the pores of the thimble. The thimble is put into a brass cell to hold it in place as shown in Figure 52.

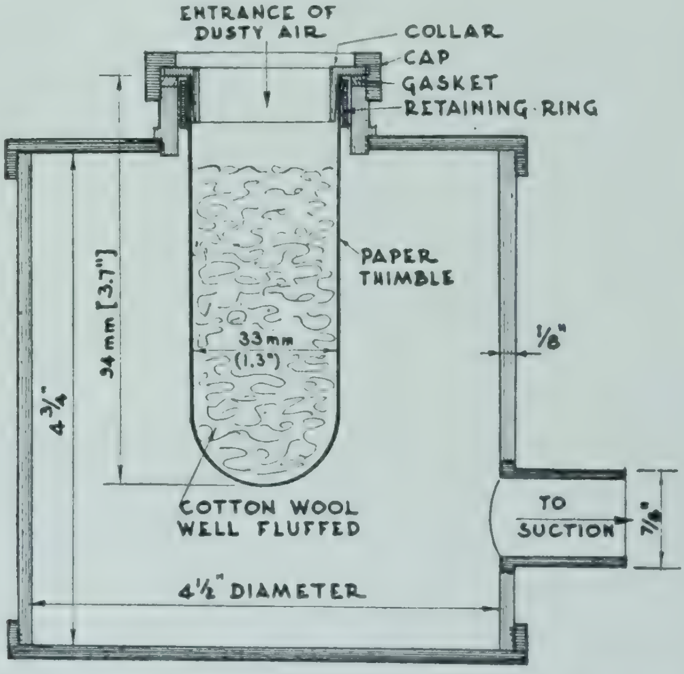

Fig. 52. Details of paper thimble and suction capsule.[38]

The dusty atmosphere is drawn through the thimble by means of suction applied through the arm in the brass cell. The dust is caught by the fluffed absorbent cotton and the thimble itself. The suction device used should be capable of sampling at the rate of about 2 cubic feet per minute and the amount of air sampled should be measured by some type of flowmeter.

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[46] L. J. Trostel and H. W. Frevert, *Ind. Eng. Chem.*, *15*, 232 (1923).

The thimbles must be tared before being used. All the thimbles should be given a preliminary drying treatment by heating in a constant temperature oven at 90 to 95° C. for 3 to 7 days. Then the drying may be completed by heating in a vacuum oven for 7 hours at 90° C., after which the thimbles are weighed as described below. A check weight should be obtained on the thimbles by exposing them to room air overnight and then redrying them in the vacuum oven at 90° C. for 7 hours. The drying may also be completed by continuing the heating in the constant temperature oven at 90 to 95° C. for two days more, which is generally sufficient to bring them to constant weight. The same drying procedure used in obtaining the tare weight is used in obtaining the dry-dust weight after sampling.

The thimbles are dried in weighing bottles and permitted to cool in desiccators. A counterpoise weighing bottle should be used in order to compensate for possible moisture condensation on the comparatively large surface of the weighing bottle. The difference in weight between the weighing bottle and the thimble before and after sampling represents the dry weight of the collected dust. This weight divided by the volume of air sampled, which is obtained by the use of the flowmeter, yields the weight of dust per unit volume, as, for instance, milligrams per cubic meter.

The paper thimble has a very high sampling efficiency. It samples large volumes rapidly and is very simple to use. It is particularly useful in the sampling of radioactive dusts. On the other hand, samples of dust collected by the paper thimble method do not lend themselves to estimation by count.

d. Resistance Pressure

The method which measures resistance pressure is really a filter-device variation. The amount of material on the filter is estimated indirectly by the increased resistance to air flow as the filter becomes clogged.

The apparatus known as the Anderson and Armspach dust determinator[47] consists of a holder in which a piece of filter paper or other porous fabric is clamped. Air is drawn through the paper at a constant rate and the difference of pressure between the two sides of the paper is determined by means of a manometer, which is connected to the holder on each side of the paper. The gauge reading indicates the difference of pressure existing between the two sides of the filter. As the paper clogs, more pressure is required to keep the air passing through at the same rate, and the manometer reading thus increases. For hygienic purposes this device is of little value for, although some correlation can be obtained between the amount of dust and the increase in pressure, neither the actual weight of the dust nor the count can be obtained.

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[47] L. Greenburg, *U. S. Pub. Health Repts.*, *40*, 765 (1925).

e. Bag Test

The bag test[48] is used for estimating "dust loading" in flues. It is especially convenient when large volumes of gas containing heavy dust loadings are to be estimated. The method consists of diverting a known volume of gas from the main gas stream and then passing this gas through a number, usually three, of dried and weighed heavy Canton flannel or unbleached muslin bags. The bags are dried and weighed after sampling and thus the amount of dust retained by the bags is ascertained. Pitot tube and temperature readings must be made at frequent intervals in order to obtain the volume of gas tested. The method is useful mainly for industrial and technical, rather than for investigational, purposes.

f. Sugar Tube

The sugar-tube method[49,50] of sampling consists of filtering 15 cubic feet of air through pure granulated sugar, which retains the dust. The sugar is then dissolved in dust-free water, leaving the insoluble dust particles in suspension. An aliquot portion of the solution is placed in a Sedgwick-Rafter cell, such as is used for counting blood corpuscles, and is examined under a microscope at 110 diameters magnification. The dust particles are counted and from this result the number of dust particles per ml. of air is computed.

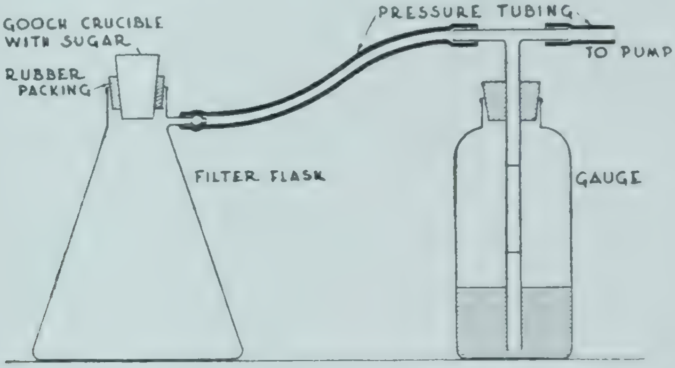

Fig. 53. Apparatus for rapid sugar tube method.

Rapid Method. A rapid modification of the sugar-tube method has been devised by McNair and Hirst.[51] The dust is collected by aspirating a measured volume of the air to be examined, 5 to 10 cubic feet being usually sufficient, through a Gooch crucible (Fig. 53) with small holes, packed with 5 g. of clean powdered sugar.

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[48] H. Bubar, *Dust Problems*, Dust Recovery, New York, 1930.

[49] A. C. Fieldner, S. H. Katz, and E. S. Longfellow, *U. S. Bur. Mines, Tech. Pap* *278* (1921).

[50] S. H. Katz, G. W. Smith, and W. M. Myers, *J. Ind. Hyg.*, *8*, 300 (1926).

[51] L. C. McNair and J. F. Hirst, *J. Ind. Hyg.*, *11*, 336 (1929).

The prepared Gooch crucible is fitted to an ordinary adapter and filter flask. The air is drawn through the packing of sugar. On completion of the sampling, the sugar is dissolved in water and the sugar solution together with the occluded dust, which is now in suspension, is washed into a centrifuge tube (Fig. 50). The centrifuge tube is about 18 cm. long and 2 cm. in diameter. To the bottom of the centrifuge tube, 3 cm. of thick-walled tubing of 1 mm. bore is attached. In order to facilitate the measurement of the dust, about 0.1 g. of red lead is suspended in alcohol and is centrifuged in the tube prior to centrifuging the sample. This procedure eliminates inaccuracies of the tube end and provides a horizontal, conspicuously colored surface from which to measure the height of the dust column. After pouring off the alcohol, the sugar solution is transferred to the tube and centrifuged for 2 minutes at 2,000 revolutions per minute. The height of the column is then measured on the graduated scale of the capillary section of the tube or is ascertained by means of a traveling microscope. The tubes should be calibrated by weighing out quantitatively 1 to 5 mg. of the particular dust being tested and then centrifuging from similar sugar solutions. The relationship is not a linear one.

The greatest disadvantage of the sugar-tube method is the difficulty of obtaining dust-free sugar, or even uniformly dusted sugar so that a correction may be applied. Nevertheless, the method is simple and will serve in many instances to give an adequate measure of dust contamination in the atmosphere.

g. Salicylic Acid Filter

Another type of filter using a porous pad is described by Matthews.[52–54] This filter is primarily intended to obtain samples of the order of 20 to 500 mg. for quantitative analysis. The samples are collected in a relatively short time, say 1 to 6 hours, so that working conditions, temperature, humidity, etc., are fairly constant. The differences in the composition of the dust attributable to these factors can be determined if necessary. This type of filter is designed to give almost complete retention of the dust, so that the mass concentration of dusts may be determined.

Reagent-quality salicylic acid is sieved through a 40-mesh sieve, those of the size of 40 mesh being used. Finer crystals are more resistant to flow and coarser crystals are not so retentive of dust. The crystals are packed on stainless-steel gauzes (*A* Fig. 54). There are three stainless-steel gauzes—two coarse-mesh gauzes with a fine-mesh gauze in between.

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[52] H. V. A. Briscoe, J. W. Matthews, P. F. Holt, and P. M. Sanderson, *Trans. Inst. Mining Met., 46,* 145 (1936).

[53] J. W. Matthews, *Analyst, 63,* 467 (1938).

[54] H. H. Watson, *J. Chem. Met. Mining Soc. S. Africa, 37,* 166 (1936); *Analyst, 62,* 232 (1937).

The coarse-mesh gauzes give the arrangement rigidity. These meshes are screwed into position in the holder by means of a spoked support (*B*) made of ebonite. The holder itself is also made of ebonite.

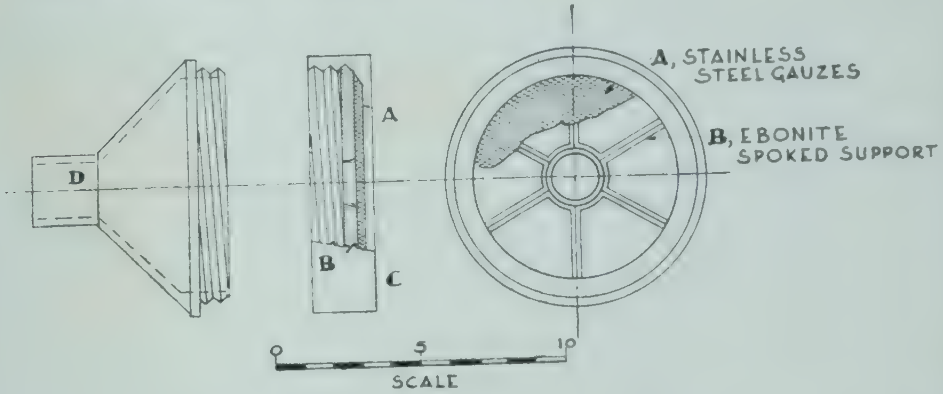

Fig. 54. Salicylic acid filter holder.

A filter cell, 7 cm. in diameter, requires 10 g. of salicyclic acid to give a pad thickness of about 4 mm. This thickness is sufficient to provide good retention without obstructing the flow. As sampling is continued, the filter clogs with the dust it retains, thus cutting the flow to a negligible amount. Hence it can be used to obtain only small samples.

For transportation the prepared cell is covered with a flat cellophane lid and may then be handled freely. Before the dust is sampled, the crystals are shaken back over the whole surface and gently pressed into position again. The cell is fitted to its support horizontally, the cellophane is removed, and the suction started. The greater the suction, the more efficient the filter. When the suction is on, the filters are very stable and sampling may be carried out in any position.

When sampling is completed the pads are covered with cellophane and the whole filter returned to the laboratory. The entire salicylic acid pad, together with the dust, is transferred to a centrifuge tube, a 50-ml. tube for 10 g. of salicylic acid, and the salicylic acid is removed by treatment with absolute alcohol. The dust is then air-dried and is in a suitable condition for chemical analysis or petrographic examination. (See Chapter VI, Section 4.)

Other variations of methods in which the dust is trapped in or on a material that can subsequently be volatilized or dissolved are the use of volatile materials like benzoic acid, anthracene, and naphthalene,[55] or the use of nitrocellulose[56] or collodion[57] in special solvents.

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[55] J. W. Matthews and H. V. A. Briscoe, *Trans. Inst. Mining Met.*, *44*, 11 (1934).
[56] P. Fritzsche, *Z. anal. Chem.*, *37*, 92 (1898).
[57] M. Hahn, German Patent 201,789 (1907).

h. Filter Paper

By use of lintless, hardened filter paper of high wet strength[58] for fine precipitates, dust can be trapped and subsequently resuspended for estimation. Results obtained by this method are said to be comparable to those obtained by impingement methods. A comprehensive review of filter-paper methods is given by Brown. This method lends itself to direct counting of the dust as in the impinger method (see page 144), to estimation by light transmission methods, or to an evaluation of the amount of dust by length of time of return of the pump handle. The efficiency of this method is greater than that of the impinger for the collection of metal fumes such as those of cadmium, lead, mercury, and zinc, and for collecting fine particles of dust.

The filter-paper sampler consists of a hand-operated, single-action pump capable of drawing 283 ml. (0.01 cubic foot) of air per stroke through filter paper and a paper holder. The pump is equipped with a ball-type check valve, which prevents air from being pushed back through the filter paper on the return stroke, and with a counter for counting the strokes. The plunger has a leather cup-type gasket. By means of an adjustable stop on the pump rod, the volumes of air drawn in per stroke can be regulated. Ten strokes per minute with a pump of the volume stated will sample 0.1 cubic foot per minute, which is equivalent to the sampling rate of the midget impinger.

The filter-paper holder consists of two flat metal surfaces. Whatman No. 50, 5.5-cm. filter paper is placed in a case equipped with removable covers in the laboratory to avoid soiling the paper. In use the cover of the case is removed and the case is screwed on to the pump. The second cover is removed and the light transmission is taken if desired. In sampling, the pump is drawn out smartly, held for several seconds to make certain that all the air passes through the filter paper and equilibrates the air pressure, and then returned for the next stroke. Light transmission can be taken again after sampling is complete.

To count the dust, remove the filter paper from the holder in the laboratory and shake in a dust-free liquid. The estimation can then be made as in the case of impinger sampling. (See page 144.)

Silverman and Ege[59] constructed a field filter-paper sampling device for sampling lead fume from a hand vacuum blower, a filter-paper holder, and a U-tube manometer. Air flow was controlled by means of a pinch clamp on the blower discharge. The holder, of brass tubing and sheet brass, is made to press-fit the blower. It is fitted with a heavy wire-mesh grille to support the filter paper and with six bolts on which the cover, also equipped with a wire guard, can be clamped by means of six wing nuts. This arrangement enabled one to change easily the 125-mm. Whatman No. 44 or 42 filter paper used for sampling. Single filter papers had a mean collection efficiency of 86.7 per cent at sampling rates of 27.7 to 48.9 liters per minute, while double filter papers had a mean collection efficiency of 98 per cent at flow rates of 3.5 to 29.0 liters per minute.

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[58] C. E. Brown, *U. S. Bur. Mines, Rept. Invest. 3788* (1944).

[59] L. Silverman and J. F. Ege, Jr., *J. Ind. Hyg. Toxicol., 25,* 185 (1943).

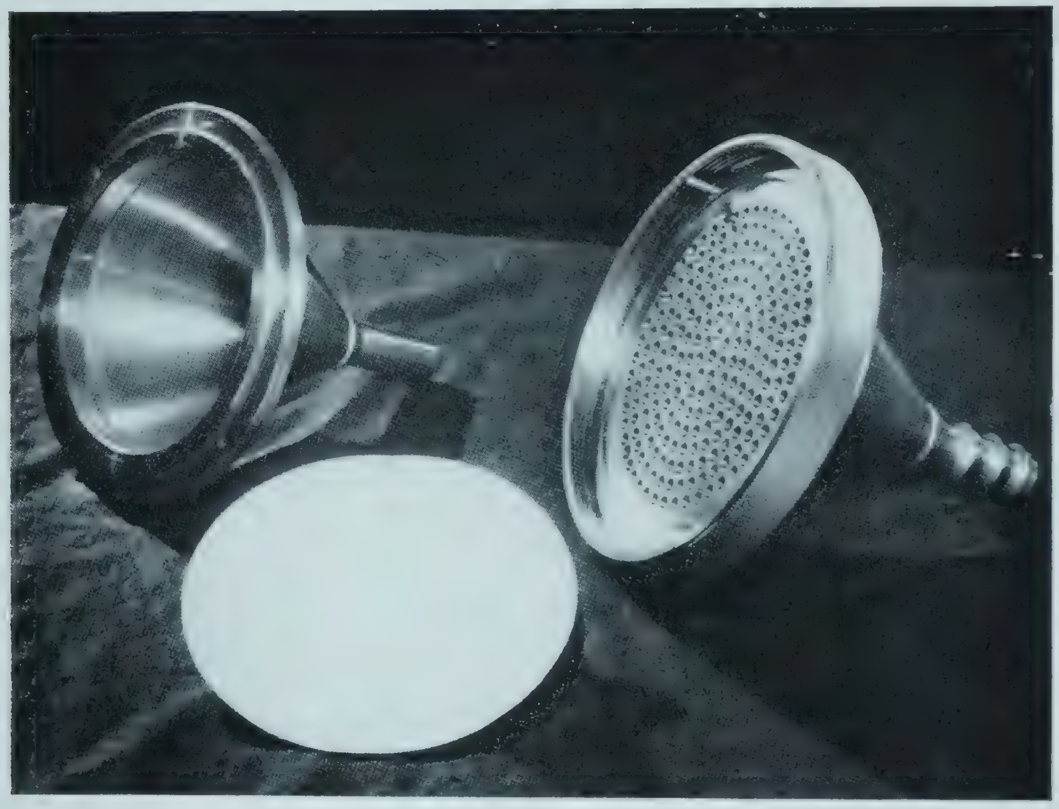

Fig. 55. Lead fume-sampling apparatus disassembled.

Bayrer and Hough[60] modified the aforementioned device by use of two funnels clamped together, as in an original design of Silverman and Ege, but they connected the collecting head to the suction device by tubing so that the head could be held in the sampling zone.

The amount of lead caught on such filter papers can be determined by direct weighing if the papers are equilibrated,[61,62] or by ashing and weighing, or by methods detailed in Chapter VII, page 195 *et seq.*

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[60] O. D. Bayrer and W. A. Hough, *J. Ind. Hyg. Toxicol.*, *27*, 89 (1945).

Another device using filter paper for the rapid sampling of large volumes of air of the order of 55 to 65 cubic feet per minute is described by Silverman and Williams.[63]

i. Miscellaneous Devices

Harrold[64] and his co-workers devised a packed-tube collector for their studies of the toxicity of lead chromate. This collector was designed to be worn by a person on the job. It consists of a tight-fitting face piece to which was sealed a rubber tube holding a glass tube 4 to 5 inches long and 0.5 inch in diameter, and having three constrictions. The glass tube was packed with successive layers of glass wool, sodium bicarbonate, 3 inches of glass beads wet with 2 ml. of nitric acid (1:1), and another layer of glass wool. The nitric acid serves to trap the lead and the bicarbonate is used to neutralize any acid vapors given off by the acid layer. This collection tube proved to be superior to the electrical precipitator. It had a resistance of 80 mm. at 32 liters per minute and 40 mm. at 14 liters per minute. The contents of the tube can then be analyzed in conventional ways.

Using a glass tube 30 cm. by 38 mm. packed with dry Pyrex glass wool, Keenan and Fairhall[65] found that lead fume was quantitatively retained.

A device used by Dudley for trapping selenium-bearing dusts is described on page 269.

7. *Impingement*

Many of the most successful instruments used in the determination of dust in industrial-hygiene studies are those based on the principle of impingement. In these devices, the dust-laden air is drawn or driven at a high velocity against a prepared surface and is thus trapped on the prepared surface itself, or is absorbed by some medium such as water. Of these types of instruments, the konimeter, the Owens jet dust counter, and the Greenburg-Smith impinger and its modifications are the more important.

[61] S. H. Katz and G. W. Smith, *U. S. Bur. Mines, Rept. Invest. 2378* (1922).

[62] W. P. Yant, E. Levy, R. R. Sayers, C. E. Brown, C. E. Traubert, H. W. Frevert, and K. L. Marshall, *U. S. Bur. Mines, Rept. Invest. 3585* (1941).

[63] L. Silverman and C. R. Williams, *J. Ind. Hyg. Toxicol.*, *28*, 21 (1946).

[64] G. C. Harrold, S. F. Meek, G. R. Collins, and T. F. Markall, *J. Ind. Hyg. Toxicol.*, *26*, 47 (1944).

[65] R. G. Keenan and L. T. Fairhall, *J. Ind. Hyg. Toxicol.*, *26*, 241 (1944).

a. Konimeter

The konimeter originally developed by R. N. Kotzé is a hand-size instrument.[66-68] It consists essentially of a valveless cylindrical suction pump with a piston of the leather-cup type and a brass dial (Fig. 56).

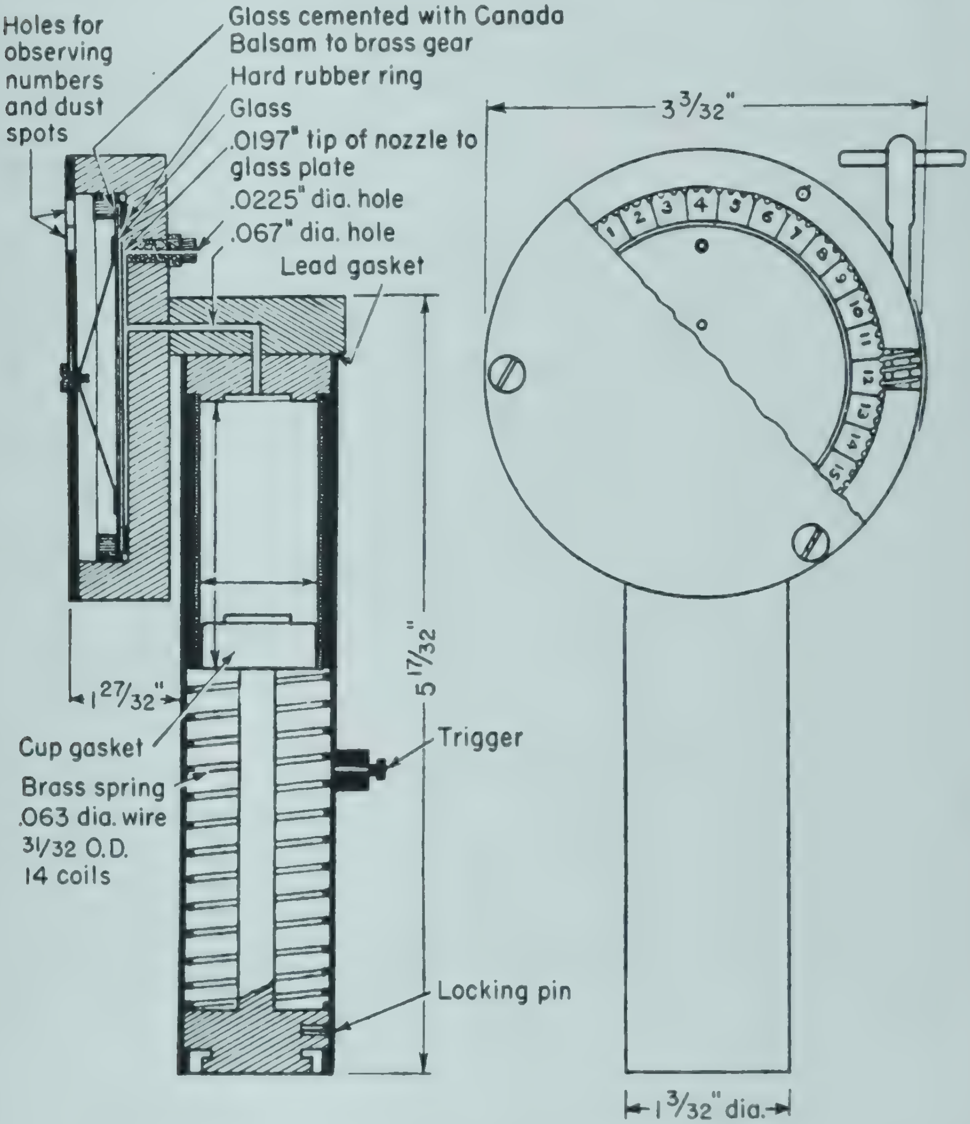
Holes for observing numbers and dust spots
Glass cemented with Canada Balsam to brass gear
Hard rubber ring
Glass
.0197" tip of nozzle to glass plate
.0225" dia. hole
.067" dia. hole
Lead gasket
3 3/32"
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
1 27/32"
5 17/32"
Cup gasket
Brass spring .063 dia. wire 31/32 O.D. 14 coils
Trigger
Locking pin
1 3/32" dia.

Fig. 56. Details of the konimeter device.[67]

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[66] J. Innes, *J. Chem. Met. Mining Soc. S. Africa*, *19*, 132 (1919).
[67] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service*, *Bull. 217* (1938).
[68] R. M. Thomson, *J. Ind. Hyg.*, *7*, 385 (1925).

The piston of the pump is actuated by a spring that insures uniform operation. It draws into the cylinder 2.5, 5.0, or 10 ml. of air at a high velocity through a nozzle which is about 0.6 mm. in diameter. The nozzle is held about 0.5 to 0.6 mm. above a glass plate, coated with a thin layer of petrolatum, glycerine jelly, mineral oil, or other adhesive film. The nozzle is protected from being clogged by large particles by a 250-mesh screen. The glass plate, cemented in a metal rim, is held by the brass dial chamber and may be revolved so that a fresh surface may be exposed to each sample. The dial is divided into 30 sectors, each one of which is numbered so as to record each sample taken. At most only 26 samples are taken, leaving at least 4 blank, usually 1, 10, 20, and 30.

The Bureau of Mines,[69] which uses the konimeter as an adjunct of the impinger, describes methods for checking the volume of air sampled by means of a microburette.

To prepare the konimeter for use, check to see that the plunger moves smoothly and that the screen and nozzle are clear. Clean the disk, using mild soap and water, by scrubbing with a camel's-hair brush or with the fingers. Rinse thoroughly, dry, polish with clean linen, and brush in one direction with a camel's-hair brush. If the humidity is low and dust and lint are held on the glass by static charges, breathe lightly on the disk to assist in removing these particles.

Apply an adhesive film to the sample side of the glass plate. The Bureau of Mines[69] recommends a mixture made from 1 ounce of glycerine jelly used for microscope work and 1 ounce of glycerol with 10 to 20 drops of water. Use less water in hot weather than in cold weather. Heat the components in a bottle held in hot but not boiling water until the jelly melts and mixes completely with the water and glycerol. Allow the mixture to cool and set to a soft jelly.

Prepare sample disks in an atmosphere as free from dust as possible. Hold the sampling side of the plate down while the adhesive is applied to avoid deposition of atmospheric dust. Use the index finger to apply the jelly to the sample disk. Wash the hands thoroughly in warm water, hold the index finger and thumb in cold water to close the pores, dry with a linen cloth, and brush to remove lint. Hold a piece of jelly about $^1/_{16}$ inch in diameter between the thumb and finger until it softens, and spread on the sample disk with the index finger, turning the disk with a sweeping circular motion. Do not rub the jelly between the fingers, as small bubbles that form in the jelly cannot be removed and may be confused with dust particles. Breathe gently on the disk until the jelly has taken up enough moisture to spread and thus remove the streaks left by the finger ridges. Examine the disk under the microscope, and if there are more than 8 to 10 particles per field, clean and prepare the disk over again. Place the disk on the konimeter with the adhesive side toward the orifice, or in a special metal carrying box, adhesive side down, if it is to be used at a later time. Place the threaded rim over the disk on the konimeter and turn until the rubber gasket makes good contact.

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[69] J. B. Littlefield, C. E. Brown, and H. H. Schrenk, *U. S. Bur. Mines, Inform. Circ. 6993* (1938).

To obtain a sample of dust, push the piston inward until it is caught and held in place at the 2.5-, 5.0-, or 10-ml. mark by a locking pin. Hold the orifice at the back of the konimeter at the sampling point and procure a sample by pressing the trigger, which releases the spring. Air rushes in through the nozzle at a high velocity, impinging its dust content in the glycerine jelly or petrolatum film on the glass plate and forming a dust spot about 1 mm. in diameter. To obtain another sample, turn the pinion to bring the next sector into position and cock the piston again. Examine the dust spot under a microscope at 200 diameters magnification and count the visible particles, as described on page 149. The results are expressed as number of particles per ml. of air.[70]

Some konimeters are equipped with a small microscope so that the dust samples obtained may be counted directly.[71]

The konimeter is one of the simplest and most compact of dust-sampling instruments. It has the advantage that it can be used very effectively to obtain grab samples and that 26 samples can be obtained on one plate. The other 4 sectors are used for blank determinations. Because of its ability to take grab samples, fluctuations in dust content can easily be sampled. It works best in atmospheres of low or medium dust content. Its disadvantage is that it has a low sampling efficiency in very dusty atmospheres, that it takes only an instantaneous sample of 2.5, 5.0, or 10 ml., and that the dust can be evaluated only in number of particles. The konimeter is well adapted to taking samples of oil- or fat-bearing dust particles such as the dust in a fur-felting industry.[72]

Minnesota Dust Counter. The Minnesota dust counter[73] is a device related to the konimeter in that the adhesive-impingement principle is used. It has, however, a moving slide upon which five to six samples may be taken and a fixed orifice. A hand pump is used to give the vacuum required for the air sample.

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[70] S. H. Katz, G. W. Smith, and W. M. Myers, *J. Ind. Hyg.*, *8*, 300 (1926).

[71] J. S. Haldane and J. I. Graham, *Methods of Air Analysis*, Griffin, London, 1935.

[72] R. R. Sayers, P. A. Neal, R. R. Jones, J. J. Bloomfield, J. M. DallaValle, and T. I. Edwards, *U. S. Pub. Health Service, Bull. 234* (1937).

[73] F. B. Rowley and R. C. Jordan, *J. Ind. Hyg. Toxicol.*, *25*, 293 (1943).

b. Owens Jet Dust Counter

The Owens jet dust counter[74–76] is a device that depends upon the combined principles of impingement and condensation. A high-velocity jet of air is caused to strike a microscope cover glass; the effect of this high velocity is to bring about a fall of pressure in the jet, accompanying which, and resulting from it, is a corresponding fall of temperature. This in turn causes a condensation of the moisture in the air upon the dust particles, which are thus projected wet against the cover glass, and, as the water evaporates, are left behind adhering to the glass.

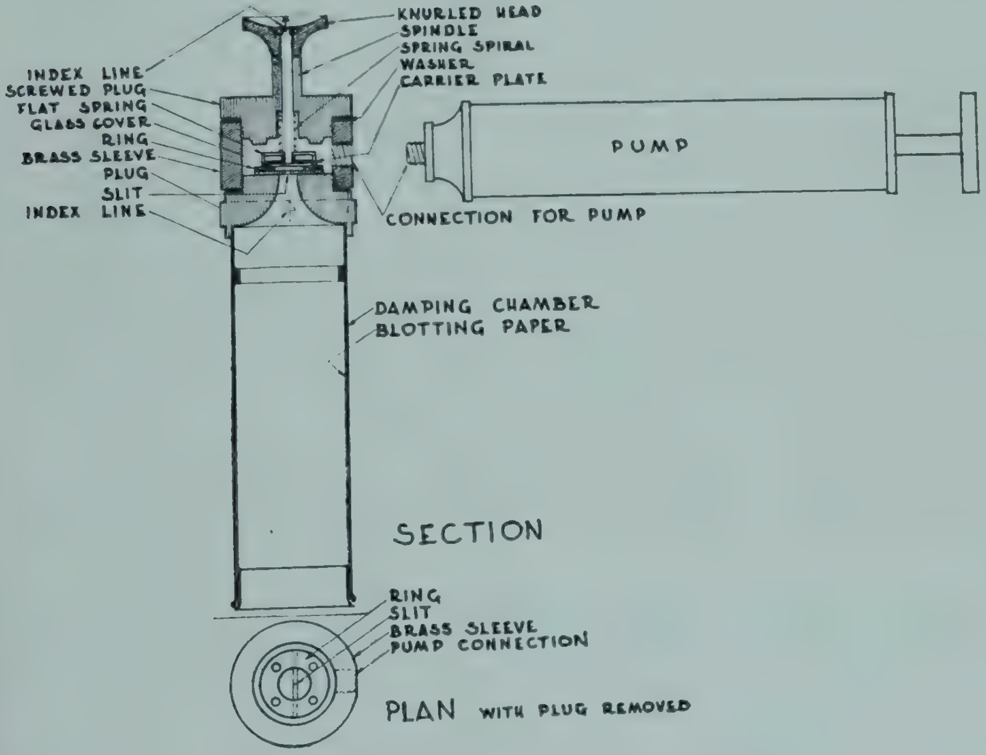
KNURLED HEAD
SPINDLE
SPRING SPIRAL
WASHER
CARRIER PLATE
INDEX LINE
SCREWED PLUG
FLAT SPRING
GLASS COVER
RING
BRASS SLEEVE
PLUG
SLIT
INDEX LINE
PUMP
CONNECTION FOR PUMP
DAMPING CHAMBER
BLOTTING PAPER
SECTION
RING
SLIT
BRASS SLEEVE
PUMP CONNECTION
PLAN WITH PLUG REMOVED

Fig. 57. Details of the Owens jet dust counter.

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[74] J. S. Owens, *J. Ind. Hyg.*, *4*, 522 (1923).

[75] J. E. Ives, R. H. Britten, D. W. Armstrong, W. A. Gill, and F. H. Goldman, *U. S. Pub. Health Service, Bull. 224* (1936).

[76] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1938).

The Owens jet dust counter consists of a damping chamber communicating through a narrow slit with an air pump, operated at right angles to the chamber (Fig. 57). The air pump has a capacity of 50 ml. The damping chamber is lined with moist blotting paper. The capacity of the damping chamber is two or three times that of the pump. When the dust in the air is to be sampled, the damping chamber is unscrewed from the instrument, passed through the air to be sampled, and replaced, the plunger of the pump being left pushed in.

A cover glass is then placed behind the slit and the pump plunger is pulled out smartly so as to draw one or more volumes of air through the slit. The rapid expansion of the air drawn through the slit lowers its temperature, it becomes supersaturated, and water condenses on the dust particles in the air. When the pump plunger is pulled out the air passes at high velocity through the narrow slit and impinges upon the cover glass. The air is deflected but the particles of water containing the dust strike the cover glass and adhere to it. The water subsequently evaporates, as the velocity falls off and the pressure and temperature again rise, and the dust particles are left on the cover glass. The narrow slit is 1 cm. long and the cover glass is placed at about 1 mm. from it. This leaves a sample of dust in the shape of a fine ribbon about 1 cm. long and about 0.2–0.4 mm. wide.

The cover slide may then be cemented to a microscope slide and may subsequently be examined under the microscope with an oil-immersion objective having a magnification of approximately one thousand diameters.

The Owens jet dust counter is a light instrument, simple to use. It is particularly useful in air-pollution studies of smoke contamination. Its disadvantages are that it can only be used for the counting of dust particles; it cannot be used for the sampling of industrial dust of high concentrations, for in this case the dust record is so thick that it cannot be counted; and it is only capable of obtaining instantaneous samples. A modification of this instrument as described by Hatch and Thompson[77] is designed so that eight slides can be used.

The Bausch and Lomb[78] dust counter is in principle an Owens jet dust counter with several modifications.

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[77] T. Hatch and E. W. Thompson, *J. Ind. Hyg.*, *16*, 93 (1934).

[78] S. W. Gurney, C. R. Williams, and R. R. Meigs, *J. Ind. Hyg. Toxicol.*, *20*, 24 (1938).

c. Greenburg-Smith Impinger[79-84]

The Greenburg-Smith impinger is the standard instrument in the United States for the collection of dusts.[85,86] It is also widely used for the collection of fumes and mists. Its efficiency for certain types of fumes, such as lead[87] and mercury, is low and variable, but nevertheless agrees reasonably well with that of the electrical precipitator.

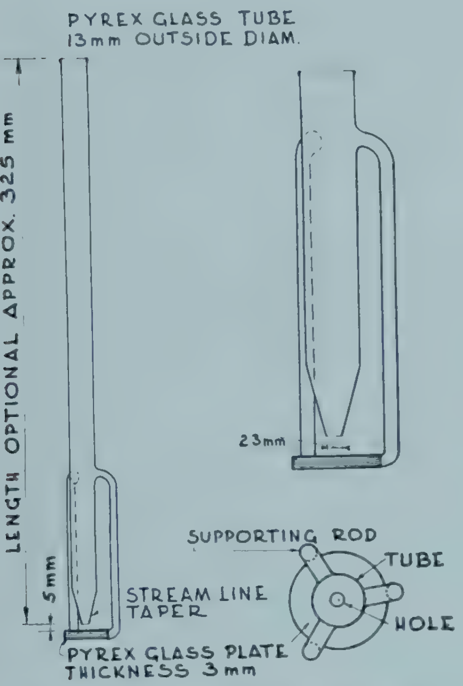
PYREX GLASS TUBE
13mm OUTSIDE DIAM.
LENGTH OPTIONAL APPROX. 325 mm
5mm
STREAM LINE TAPER
PYREX GLASS PLATE THICKNESS 3mm
23mm
SUPPORTING ROD
TUBE
HOLE

Fig. 58. The Greenburg-Smith impinger.

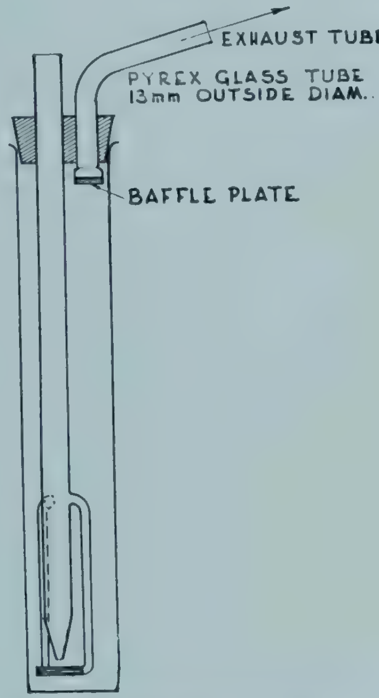
EXHAUST TUBE
PYREX GLASS TUBE
13mm OUTSIDE DIAM.
BAFFLE PLATE

Fig. 59. Impinger tube and collection tube assembled.

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[79] L. Greenburg and G. W. Smith, *U. S. Bur. Mines, Rept. Invest., 2392* (1922).
[80] S. H. Katz, G. W. Smith, W. M. Myers, L. J. Trostel, M. Ingels, and L. Greenburg. *U. S. Pub. Health Service, Bull. 144* (1925).
[81] L. Greenburg and J. J. Bloomfield, *U. S. Pub. Health Service, Reprint 1528* (1935).
[82] C. E. Brown and H. H. Schrenk, *U. S. Bur. Mines, Inform. Circ. 7026* (1938).
[83] J. J. Bloomfield and J. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1938).
[84] J. J. Bloomfield, *Am. Pub. Health Assoc. Yearbook 1935–36*, p. 86.
[85] *Am. Pub Health Assoc. Yearbook 1930–40*, p. 92.
[86] *Ind. Hyg. Newsletter, 7*, No. 5, 15 (1947).
[87] J. B. Littlefield, F. L. Feicht, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3401* (1938).

The Greenburg-Smith impinger is a device through which air is sampled at a high velocity. The air is impinged at this high velocity against a glass plate which is immersed in an absorption medium. The dust particles are momentarily arrested by the impinging process, are wetted by the water or the absorption liquid, and thus are trapped. The Greenburg-Smith impinger also acts as an absorber and traps any gases or liquids which are soluble in water or in the other absorption mediums used.

The impinger tube (Fig. 58) is made entirely of glass. It consists of a piece of Pyrex glass tubing 13 mm. in outside diameter, about 32 cm. long, having a tip drawn to a 2.3-mm. orifice. At the end of the tube, attached to it by three supporting arms, is a circular plate of glass. 25 mm. in diameter and set in place at exactly 5 mm. from the orifice of the tube. The impinger tube may be set in a cylinder (Fig. 59) or a 500-ml. wide-mouth flask. Sufficient liquid must be in the vessel to cover the impinger plate to a depth of approximately 3 cm. In large tubes or cylinder-type vessels, 100 ml. is generally sufficient. In the 500-ml wide-mouth flasks, 225 to 250 ml. of the absorbing liquid is necessary. During winter or when cold air is being sampled, it may be necessary to

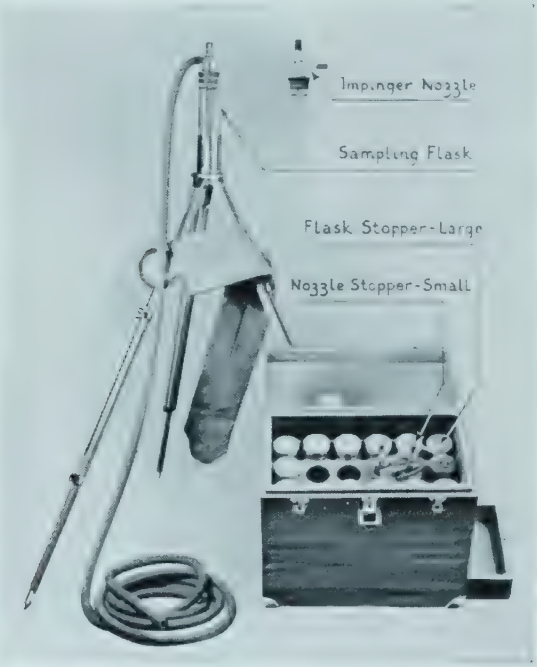

Fig. 60. Impinger apparatus.
(*Courtesy Willson Products, Inc.*)

heat the liquid in the impinger flask in order to keep it from freezing. Ives[75] and his co-workers used an electric lamp in a box, keeping the impinger flask in the box. Other solvents such as ethyl, *n*-propyl, or isopropyl alcohol can be used for the same purpose. These solvents also reduce the risk of solubility of the dust in water.

The Greenburg-Smith impinger apparatus needs some device to draw the air in with sufficient velocity to impinge against the plate. Electric suction, compressed-air suction, and hand-driven suction devices are all used in connection with the impinger. Sufficient suction must be developed to give a sampling rate of 1 cubic foot per minute. With a standard orifice immersed, as mentioned, to a depth of 3 cm., this flow rate will be obtained at 3 inches of Hg negative pressure. Greater speeds than that are likely to disturb the trapping liquid so violently as to expel it from the flask. A gas-measuring device of some type may also be in the line and should be calibrated so that one may control the rate and quantity of air sampled; however, the standard orifice is an excellent metering nozzle and by using an air-bleeding device and a vacuum gauge

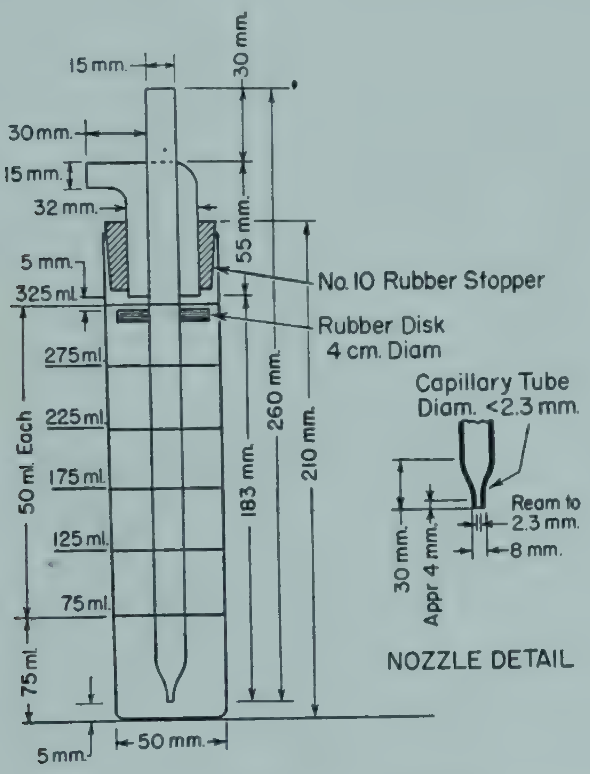
15 mm.
30 mm.
30mm.
15 mm.
32 mm.
5 mm.
325 ml.
275 ml.
225 ml.
175 ml.
125 ml.
75 ml.
50 ml. Each
75 ml.
5 mm.
50 mm.
55 mm.
183 mm.
260 mm.
210 mm.
No. 10 Rubber Stopper
Rubber Disk
4 cm. Diam
Capillary Tube
Diam. <2.3 mm.
Ream to
2.3 mm.
8 mm.
30 mm.
Appr 4 mm.
NOZZLE DETAIL

Fig 61. Modified impinger.[62]

to maintain the negative pressure, the air-flow rate of 1 cubic foot per minute can be maintained. The standard orifice can also serve as a critical orifice, as at any suction pressure the maximum air-flow rate obtainable is 1 cubic foot per minute.

Modified Impinger. A more compact and convenient impinger flask and nozzle have been developed by Hatch, Warren, and Drinker.[88] The modified impinger (Fig. 61) does away with the glass impinging plate and utilizes the bottom of the trapping flask for this purpose. The suction connection is combined with the inlet tube, thus simplifying the device still further. The essential parts of this modification are a straight piece of Pyrex tubing, 15 mm. in outside diameter and approximately 275 mm. in length. The tube is drawn down in streamline form at its lower end to a tip with a 2.3-mm. orifice. In sampling this orifice is kept approxi-

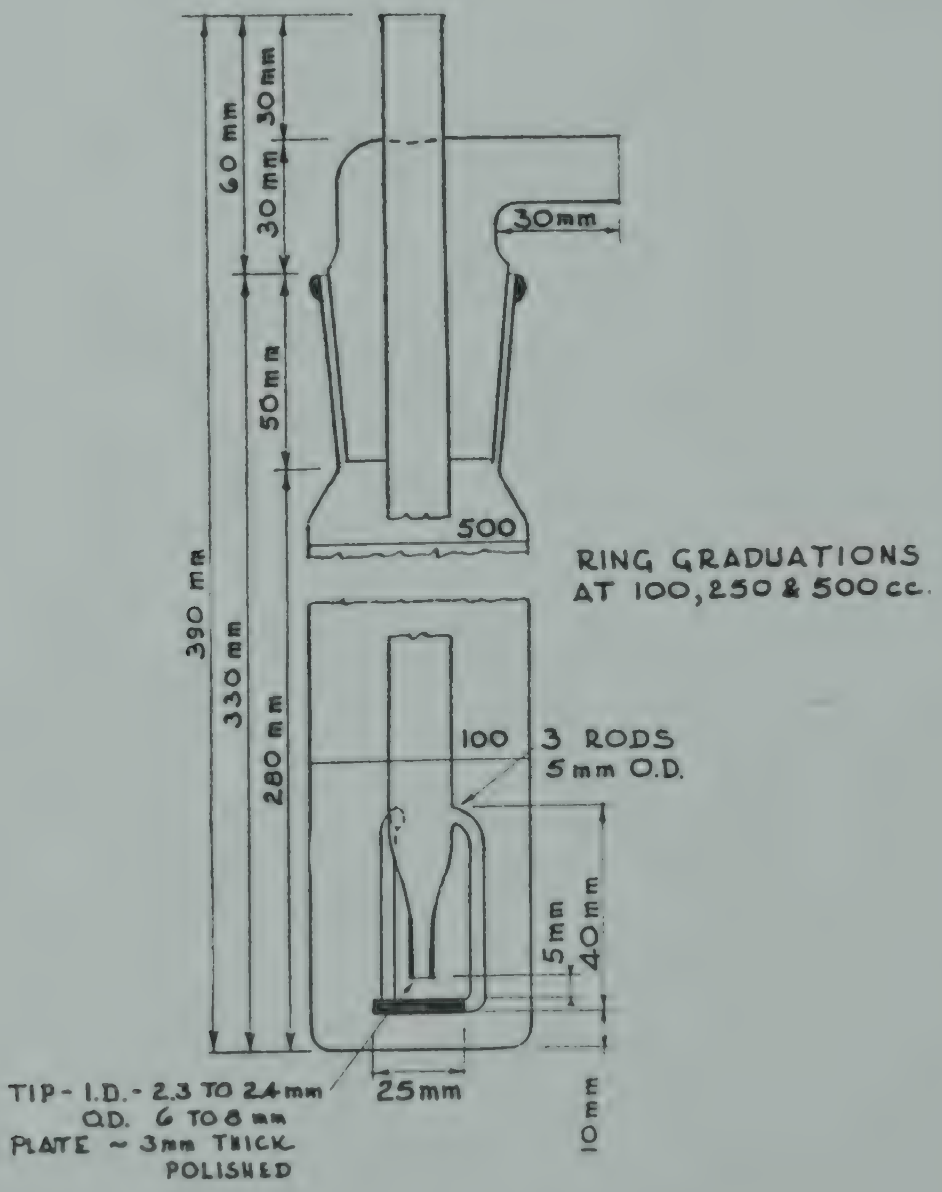
60 mm
30 mm
30 mm
30mm
50mm
500
RING GRADUATIONS
AT 100, 250 & 500 cc.
390 mm
330 mm
280 mm
100
3 RODS
5 mm O.D.
5mm
40 mm
25mm
10 mm
TIP - I.D. - 2.3 TO 2.4 mm
O.D. 6 TO 8 mm
PLATE ~ 3mm THICK
POLISHED

Fig. 62. All-glass impinger.

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[88] T. Hatch, H. Warren, and P. Drinker, *J. Ind. Hyg.*, *14*, 301 (1932).

mately 5 mm. from the bottom of the flask, a guide line on the flask indicating this distance. The flask is a cylinder 50 mm. in diameter and 210 mm. in height. It requires a fluid volume of only 75 ml. to give the proper depth of immersion to the nozzle. An entrainment trap in the form of a rubber ring prevents the possible loss of the liquid, and possibly dust, with the outgoing air.

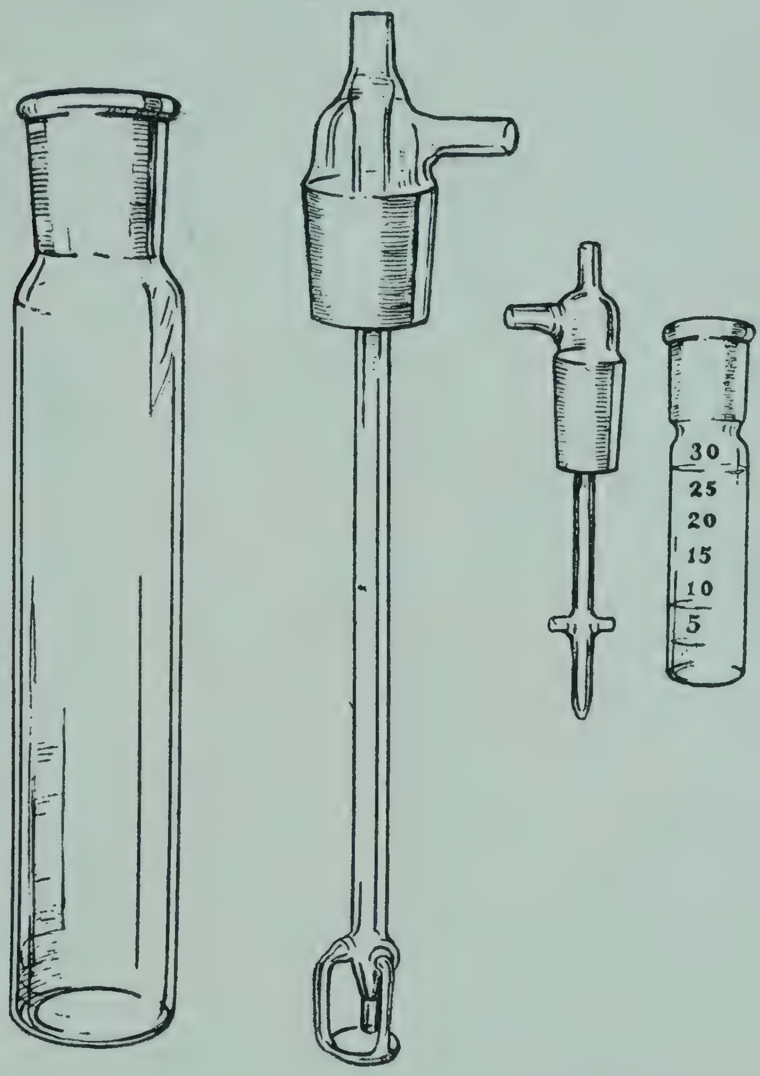

Fig. 63A. All-glass impinger and midget impinger.

The cylinder-type impinger flasks may be placed in a leather holster, which may be suspended from the shoulders of a worker and strapped to his chest.[89,90] This enables an investigator to take a sample of air very close to the locations or positions that a worker occupies during his work.

All-Glass Impinger.[91] An impinger has been constructed which embodies the best features of the Greenburg-Smith and Hatch impingers. This is an all-glass Pyrex impinger, Fig. 63. It consists of a flat-bottom cylin-

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[89] C. Badham, H. E. G. Rayner, and H. D. Broose, *Rept. Director-General Pub. Health, New South Wales,* Serial No. 12 (1927).

[90] L. Greenburg and J. J. Bloomfield, *U. S. Pub. Health Service, Reprint 1528* (1935).

[91] J. M. DallaValle, *U. S. Pub. Health Service, Reprint 1848* (1937).

TABLE 4

Summary of Characteristics of Certain Dust-Sampling Instruments[91a]

	Characteristics								
Instrument	Principle of operation	Efficiency against industrial dusts, per cent	Application	Method of quantification	Skill in quantification	Sampling skill	Volume of sample	Advantages of instrument	Disadvantages of instrument
Impinger	Impingement	98+	General	Count, gravimetric, chemical	Considerable	Some	Any amount; rate = 1 c.f.m.	1. High sampling efficiency in either low or high dust concentrations. 2. Sample can be quantificated by counting, weighing, or chemical analysis. 3. Can be used as absorber.	1. Requires power for operation 2. Low efficiency for certain fumes.
Electrical precipitator	Electrical precipitation	100	"	"	"	Considerable	Any amount; rate = 10 to 50 l.p.m.	1. High sampling efficiency in either low or high dust concentrations. 2. Sample can be quantificated by counting, weighing, or chemical analysis. 3. Large samples obtained rapidly. 4. Very useful for fumes.	1. Requires electric power for operation. 2. Some danger from high voltages.
Paper thimble.	Filtration	100	"	Gravimetric, chemical	Some	Very little	Any amount; rate 1 to 2 c.f.m.	1. High sampling efficiency. 2. Samples large volumes rapidly. 3. Laboratory technique requires only drying and weighing for most dusts. 4. Samples may be kept indefinitely without deterioration.	1. Samples cannot be counted. 2. Drying of thimbles is a very slow process.

TABLE 4 (*continued*)

Instrument	Characteristics								
	Principle of operation	Efficiency against industrial dusts per cent	Application	Method of quantification	Skill in quantification	Sampling skill	Volume of sample	Advantages of instrument	Disadvantages of instrument
Owens jet dust counter	Jet condensation	99+	Outdoor dust and for particle-size studies	Count	Some	Very little	50 to 1,000 ml.	1. Light, simple, and quick to operate. 2. High efficiency for atmospheric smoke. 3. No power needed for operation. 4. Laboratory technique requires only a microscope.	1. Dust cannot be weighed or analyzed chemically. 2. Obtains only "grab" samples due to small sampling volume. 3. Impractical in high dust concentrations. 4. Selective action; efficient only for dusts 2 μ or less.
Konimeter	"	99+	For concentrations less than 18 million particles per cubic foot	"	"	"	10 ml.	1. Light simple and quick to operate. 2. Efficiency high for moderate concentrations. 3. No power needed for operation. 4. Laboratory technique requires only a microscope.	1. Dust cannot be weighed or analyzed chemically. 2. Obtains only "grab" samples. 3. Not practical in high dust concentrations; limited to 15 or 18 million particles, or less, per cubic foot.

[91a] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1938).

drical flask, with three graduations, 100 ml., 250 ml., and 500 ml. These graduations permit dilutions of samples to be made easily in the flask itself without the necessity of transferring to larger containers, as is usually the case. The tops of all flasks are ground uniformly for Ŧ 45/50 glass stoppers. The nozzles are equipped with fixed disks, but with much shorter supporting arms. This tends to cut down breakage, which formerly was a serious drawback to the all-glass Greenburg-Smith type of nozzle. The combination suction connection and inlet tube used on the Hatch impinger is retained, but the former now has been carefully ground so as to be interchangeable with all flasks.

This impinger is a rigid unit. There is little opportunity for the fixed disk or the supporting rods to break. The all-glass construction also makes it possible to use the device for sampling those gases, liquids, etc., which attack rubber. In addition, the complete nozzle can be immersed in caustic solutions for cleaning.

The Greenburg-Smith impinger and its modifications have many advantages. One of great importance is that it has been standardized and used by the U. S. Public Health Service. It not only acts as a dust-sampling device but also as an absorber. It is, however, a fragile instrument, it needs a strong source of power, it can rarely be used by one person alone, and it is at times exceedingly cumbersome. The other instruments described of a simpler nature can very often give equally valuable information. Table 4 gives a comparison of some of the instruments described.

d. Midget Impinger[92-94]

The midget impinger, developed by the U. S. Bureau of Mines, is a hand-cranked sampling instrument which samples at low rates of flow. It is an efficient collecting device for toxic dusts but because of its low sampling rate, of the order of 3 liters per minute, the accuracy of analyses may be less than with the large impinger. On the other hand, it can be used far more easily than the large impinger where electricity or other means of driving the air through the large impinger is not available. Its efficiency for sampling fumes is low and therefore it should not be used for this purpose. The usual sampling rate for the midget impinger is 0.1 cubic foot per minute.

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[92] J. B. Littlefield, F. L. Feicht, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3360* (1937).

[93] J. B. Littlefield and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3387* (1938).

[94] H. H. Schrenk and F. L. Feicht, *U. S. Bur. Mines, Inform. Circ. 7076* (1939).

The midget impinger flask is a flat-bottom tube, about 11 cm. long and 2.5 cm. in diameter, with a side arm 1 cm. in diameter tilted upward at an angle of 45° to facilitate emptying, dilution, and cleaning. The flask is graduated at 5-ml. intervals from 5 to 30 ml. and a mark at 5 mm. serves as a guide for setting the nozzle of the intake tube at the proper distance. The four projections at the lower end of the intake tube serve to hold it centrally in the flask. The orifice of the intake tube must be carefully adjusted to 1 mm. Generally 10 ml. of sampling fluid is used. Solvents analogous to those employed in the regular impinger are used for the midget impinger.

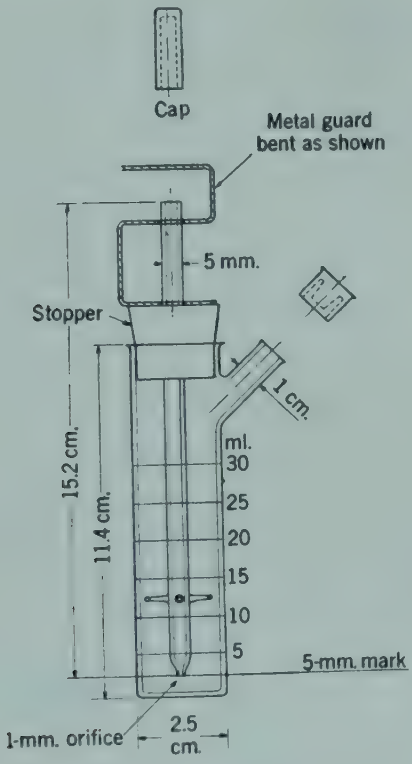

Fig. 63B. Midget impinger.

All-glass midget impingers[95] are available and these are particularly useful when a collection fluid other than water is being used. If rubber-stoppered impingers are used with nonaqueous collection media, then the samples should be transferred to all-glass containers as soon as possible.

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[95] Engineering Unit, Div. Ind. Hyg., U. S. Pub. Health Service, *Ind. Eng. Chem., Anal. Ed., 16,* 346 (1944).

The pump specially designed for this impinger has been described on page 35. The pump and impinger flasks are set in a case which can be supported by an operator by means of a shoulder strap. The flask is connected to the suction pump by $^1/_4$-inch tubing and may be placed in a small holster to be held at the sampling point. The apparatus is commercially available.

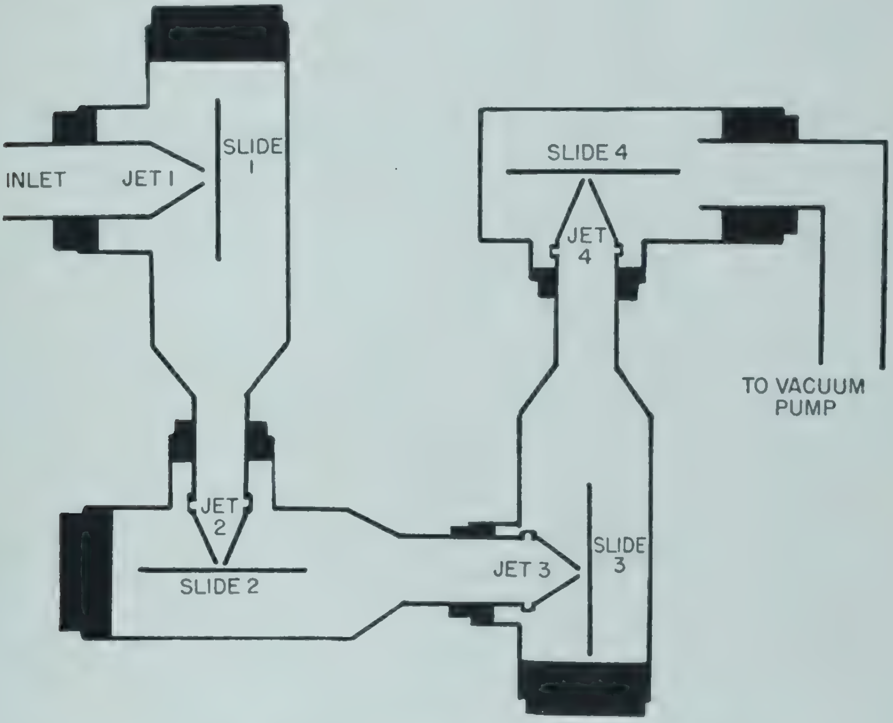

Fig. 63C. Modified cascade impactor.

Special Impinger. Another modification of the Greenburg-Smith impinger is the portable motor-driven impinger unit devised by Smith and Friis.[96] The trapping vessel is so designed as to act as an absorber. It was used particularly for sulfur dioxide estimations.

e. Cascade Impactor

The cascade impactor[97,98] is a device designed for the measurement of the particle size and concentration of airborne solid or liquid particles. This instrument consists of a series of four jets arranged perpendicularly to four glass slides at a distance of 1 mm. from each slide (Fig. 63C). The opening of each jet is made successively smaller so that when air or a gas is drawn through the device, the linear velocity increases as the gas emerges from each jet and thus particles of progressively smaller size are impacted on each succeeding slide. The size distribution can be obtained by microscopic count and by weighing the material deposited on each slide.

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[96] R. B. Smith and B. S. T. Friis, *J. Ind. Hyg.*, *13*, 338 (1931).
[97] K. R. May, *J. Sci. Instruments*, *22*, 187 (1945).
[98] L. S. Sonkin, *J. Ind. Hyg. Toxicol.*, *28*, 269 (1946).

The device made by Sonkin (Fig. 63C) consisted of four separate glass sections fitted together with rubber stoppers. The slides were held in place by indentations in the glass.

The dimensions of the jets, the air speed through the jet at flow rates of 16.5 to 17.5 liters per minute, and the approximate range of droplet size is given in Table 5.

TABLE 5

Jet Dimensions, Air Speed, and Droplet Size Obtained with Cascade Impactor[98]

Jet number	Dimensions of jet, cm.	Air speed through jet, m.p.h.	Approximate range of particle size, μ
	Cascade impactor[a]		
1	1.9 by (0.6–0.7)	5	200–10
2	1.4 by 0.16	30	20–3
3	1.4 by 0.10	50	7–1
4	1.4 by 0.06	80	3–0.7
	Modified cascade impactor[b]		
1	1.1 by 0.1	~ 60	0.7
2	0.9 by 0.08	~ 90	1.5–0.25
3	0.7 by 0.05	~180	1.1–0.15
4	0.7 by 0.02	<700	0.7–<0.1

[a] Air speed at flow rate of 17.5 liters per minute.

[b] Measurements for jet dimensions and air speed of modified cascade impactor are approximate. Air speed at flow rate of 16.5 liters per minute.

D. METHODS OF DUST EVALUATION

1. *Counting of Dust Particles*

It was explained in a previous section that one of the methods used for the estimation of dust particles is the counting of the particles and the subsequent correlation of the count with the volume of air sampled. Dust counts have a threefold application: (1) They are an index of the dustiness of a working atmosphere. (2) They help to determine the effectiveness of dust-removal equipment. (3) They can be used in conjunction with medical data to determine the threshold or safe limit of exposure to a specific dust. Dust counts are a quantitative measure of a working environment. Coupled with a knowledge of the safe or threshold limits (Tables 6 and 7, Appendix), they may be used to tell whether the atmospheric conditions found are inimical to the health of workers. DallaValle[99] recommends that dust counts be expressed as being greater or less than a maximum tolerance, such as the threshold limit, without any reference to the actual counts themselves.

a. Greenburg-Smith Impinger Samples

An estimate in an aliquot portion of a water or other solvent suspension can be made by counting the dust particles with the aid of a microscope where (1) the dust particles are caught in a medium such as water, ethyl alcohol, *n*-propyl alcohol, or isopropyl alcohol, as, for example, in the Greenburg-Smith impinger, which is the method approved by the U. S. Public Health Service; (2) the dust is absorbed or filtered out by sugar or some other solid, which can subsequently be dissolved and the dust suspended in water, as, for example, in the sugar-tube method; or (3) the dust can be shaken from a lintless hardened filter paper of high wet strength and suspended in a dust-free liquid.

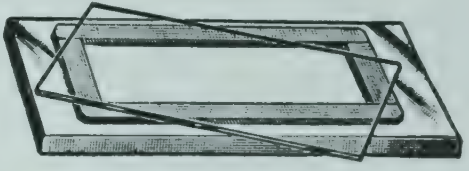

Fig. 64. Sedgwick-Rafter cell.
(*Courtesy Will Corporation*)

Greenburg and Bloomfield[100] recommended the following procedure. As soon as practicable and preferably before 24 hours have elapsed because dust particles are slightly soluble in water, remove and carefully wash the stopper of the flask in which the sampling was done. Add the washings to the contents of the flask. Filter the entire sample into a volumetric flask through a screen of approximately 325-mesh fineness. This will eliminate all particles over 40 μ, for only smaller ones will go through the filter. If the dust suspension in the volumetric flask is too dense, it should be transferred to a larger volumetric flask and diluted further, or an aliquot should be removed and diluted to a known volume. The dilution should be continued until the number of particles counted in each microscope field is about 50 to 75. Agitate the contents of the volumetric flask so that a uniform suspension is obtained. Remove two 1-ml. aliquots with a 1-ml. pipette and just fill two Sedgwick-Rafter counting cells (Fig. 64).

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[99] J. M. DallaValle, *U. S. Pub. Health Service, Reprint 2088* (1939).

[100] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1938)

A Whipple ocular micrometer disk (Fig. 65) or a modification (Fig. 67) should be used as the eyepiece. This disk has a large square engraved on it, covering a large part of the field, and this square is divided into 100 medium-sized squares. One of these is in turn further subdivided into 25 small squares. Using an ordinary microscope provided with a suitable eyepiece (7.5× or 10×) and objective (16 mm. or 10×) and fitted with an Abbe condenser, the proper tube length of the microscope is determined by calibration with a stage micrometer, so that the side of the large square of the eyepiece covers 1,000 μ [1 mm.]. The large square of the eyepiece ruling, therefore, encloses the dust in an area of 1 square mm.; and since the cell is 1 mm. deep, all the dust suspended in 1 cubic mm. of the water is under the ruled field. This examination is accomplished by raising and lowering the lens system so as to focus throughout the entire depth of the cell. As a source of illumination, an ordinary small electric microscope lamp may be used.

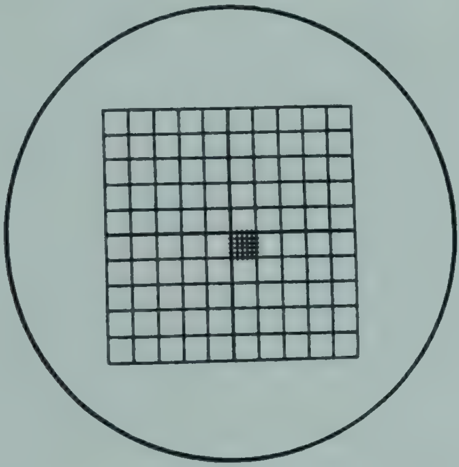

Fig. 65. Ruling of Whipple ocular micrometer disk.

The dust is permitted to settle for 20 minutes before counting is done if water is used and for 25–30 minutes with other solvents. In general, only particles less than 10 μ in diameter are counted for the reasons previously given. The inclusion of particles larger than 10 μ makes very little difference in the total count. The average diameter of a particle for the purpose of this exclusion is judged by inspection. In practice it is necessary to count the dust in only one-quarter of each ruled field, the entire field having been examined for uniformity. Such counts on 5 fields, so dispersed as to be representative, are made on each of the two Sedgwick-Rafter cells. These 10 counts are averaged, but this average is not to be taken as the final count until a corresponding control count has been subtracted. In all cases a sampling flask that has been handled in the plant, but through which no air has been aspirated, is used as the control for the particular series of samples taken in that plant on that particular day, and counts are made on this control fluid in the same manner as on the fluid through which the air sample has been impinged. The control sample takes into consideration any dust which may be present in the eyepiece micrometer, in the lenses of the microscope, in the Sedgwick-Rafter counting cell, and in the sampling liquid itself. From the average gross count obtained on the impinger sample, the average control count is to be subtracted to give the average net count per one-quarter microscopic field.

The average net count per one-quarter microscopic field is multiplied by 4 to yield the average count in the total field. Since the Sedgwick-Rafter cell is 1 mm. deep, this figure represents the number of particles in 1 cubic mm. of the diluted sample. This value is multiplied by 1,000 to give the count per ml. of sample and again by the total number of ml. of liquid to which the original sample was diluted. This product is divided by the number of cubic feet of air sampled.

To summarize, the number of particles per cubic foot of air equals the average net count per one-quarter field multiplied by a factor, where the factor equals

$$\frac{4 \times 1{,}000 \times \text{total volume of diluted sample in ml.}}{\text{Volume of air sampled in cubic feet}}$$

The average dust exposure of a worker is ascertained by multiplying the average dust concentration obtained in the count in each activity by the time spent in the atmosphere.[101]

In addition to the light-field technique detailed above, particles can be counted by a special dark-field procedure using a microscope[102] fitted with a dark-field condenser, painted with a black spot in the middle of the underside of the bottom lens of the condenser, a 16-mm. (0.25 numerical aperture) objective, and a 30× compensated eyepiece containing a micrometer outlining an area of 0.01 mm.^{2}. More particles can be seen by the dark-field procedure than by the light-field method.

[101] J. M. DallaValle, *U. S. Pub. Health Service, Reprint 2083* (1939).

[102] C. E. Brown, *U. S. Bur. Mines, Rept. Invest. 3788* (1944).

The limit of visibility[103] for counting dust in impinger and filter-paper samples by the light-field method has been found by Brown and Feicht[104] to be of the order of 0.9 μ for a microscope equipped with an objective having a numerical aperture of 0.30 and 1 μ for a microscope equipped with an objective having a numerical aperture of 0.25. Not all particles down to this size are included in a count because some of them fail to settle. In the dark-field method, using an objective with a numerical aperture of 0.30, the limit of visibility appears to be 0.4 μ, hence more particles can be counted by the dark-field procedure than by the light-field method. Counting may also be performed by means of a microprojector. (See page 156.)

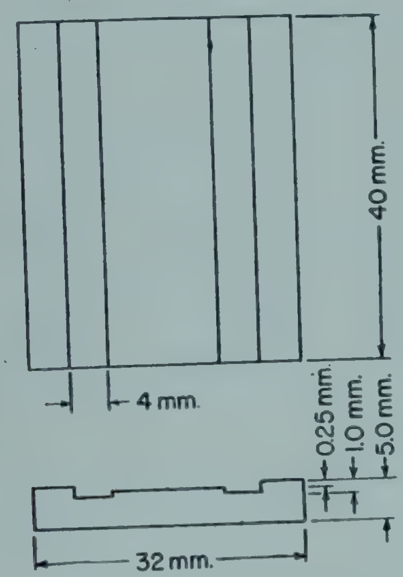

Fig. 66. Hatch one-piece counting cell.

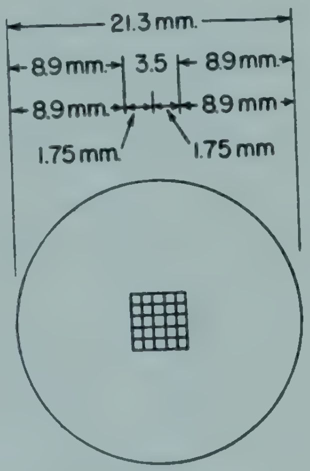

Fig. 67. Modified ocular micrometer.

Modified Counting Cells. In addition to the Sedgwick-Rafter cell other counting cells are available.[105] Hatch and Pool[106] describe a one-piece cell (Fig. 66), which has a depth of 0.25 mm. Its main advantage lies in its one-piece rugged construction. It takes less time for the dust to settle in this cell since it is $^1/_4$ as deep as the Sedgwick-Rafter cell.

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[103] E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Wiley, New York, 1938.

[104] C. E. Brown and F. L. Feicht, *U. S. Bur. Mines, Rept. Invest. 3821* (1945).

[105] C. E. Brown, R. L. Beatty, and T. B. Kirby, *U. S. Bur. Mines, Inform. Circ. 7331* (1945).

[106] T. Hatch and C. L. Pool, *J. Ind. Hyg., 16,* 177 (1934).

Williams[107] uses a Spencer "Bright-Line" haemacytometer. The cover glass is placed on glass supports, which are raised from the body of the slide as in the Hatch cell but the clearance is only 0.1 mm. Because of this depth, this cell requires practically no waiting time at all before making the counts.[108]

The Dunn[109] counting cell is made of Pyrex glass. It consists of two parts, one of which is a glass plate 1 mm. thick, ground on both surfaces, with a central hole of such a diameter that the cell will hold approximately 0.25 ml. An optical flat, polished slide completes the arrangement.

Couchman and Schulze[110] describe a circular glass-disk counting cell. The disk is held between two threaded circular metal frames. The upper frame has a central circular opening 35.6 mm. in diameter and is machined to 1 mm. thickness. The accuracy of the cell is dependent upon the latter dimension. The other dimensions need only be approximate. Its greatest advantage lies in the replaceability of the glass disk. It is also easier to clean.

Double circular cells, one a two-hole, two-piece cell having circular brass rings cemented to a microscope slide and the other a three-piece cell having two circular holes in a microscope slide, have been suggested by Brown.[111] These cells have the advantage that both of the cell parts can be filled (preferably not with the same pipetteful of sample liquid), counted, and washed at the same time.

Modified Ocular Micrometer for Dust Counting.[112] In making plankton counts, it is customary to count the whole field covered by the Whipple micrometer disk. In making dust counts, on the other hand, it is the practice to count the dust in only one-quarter of each ruled field. Only one of the three quadrants which do not contain the finely subdivided square is counted; the remaining three are unused and are therefore unnecessary. To facilitate the counting of dust samples, a micrometer similar to that shown in Figure 67 may be used. The ruled grid corresponding to one quadrant of the Whipple grid is located in the center of the visible field. The grid consists of an etched square of 3.5 mm. side measurement, divided into 25 small squares. Results obtained with this micrometer disk are identical with results obtained when counting one-fourth of the Whipple field. Calculations are made in a manner entirely analogous to that detailed for the Whipple disk.

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[107] C. R. Williams, *J. Ind. Hyg. Toxicol., 19,* 226 (1939).

[108] M. Annetts and J. D. Leitch, *J. Ind. Hyg. Toxicol., 18,* 98 (1936).

[109] K. L. Dunn, *J. Ind. Hyg. Toxicol., 21,* 202 (1939).

[110] C. E. Couchman and W. H. Schulze, *U. S. Pub. Health Repts., 53,* 348 (1938).

[111] C. E. Brown, R. L. Beatty, and T. B. Kirby, *U. S. Bur. Mines, Inform. Circ. 7331* (1945).

[112] R. T. Page, *U. S. Pub. Health Repts., 52,* 1315 (1937).

b. Counting Konimeter Samples

The konimeter glass plate upon which the samples are impinged is particularly adapted for microscope counting. The glass plate with its numbered samples is adjusted on the microscope stand with the aid of a special holder having a pinion similar to that on the konimeter. This device enables one to bring the various dust spots into view much more simply than can be done with the naked eye, for once one spot is located the others may readily be turned into position. The microscope is provided with an ocular and objective, so adjusted as to give approximately a 200-diameter magnification. An 8-mm. or 20× objective and a 10× ocular have been found to give this result. A 10-magnification (16-mm.) objective with a compensated 20-magnification eyepiece is also used.[113] A micrometer screen placed in the ocular is so designed as to have two cross lines which outline 9° sectors (Fig. 68) or 18° sectors. It is necessary for the microscopist to project imaginary lines to the center of the sectors, for these do not actually extend that far. If such lines were drawn to the center they would obscure that portion of the spot having the most particles.

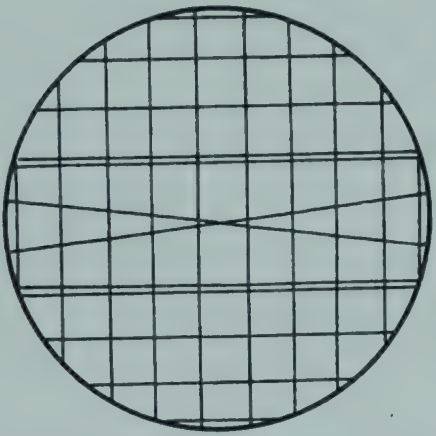

Fig. 68. Konimeter ocular micrometer.

Before the actual counting of the dust particles is begun, a blank determination is run on unused portions of the glass plate. Usually four sectors are averaged for the blank determination. This blank determination is necessary in order to obtain a count of the dust impurities in the petrolatum or glycerine jelly. It is subtracted from the sample counts. The petrolatum used in practice has a refractive index of 1.48, enabling most dusts that occur in industry to be readily visible.

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[113] J. B. Littlefield, C. E. Brown, and H. H. Schrenk, *U. S. Bur. Mines, Inform. Circ. 6993* (1938).

The dust spots are adjusted under the microscope so that the ocular sectors divide them symmetrically. All the particles in one sector are then counted; by rotating the eyepiece other portions of the spot are brought into the sector. Counting four such sectors on one spot has been found to give a representative result. Subtracting the blank and then multiplying by 10 will give the dust count in the entire spot. This factor is used because four 9° sectors have been counted, which gives a total of 36°. Ten times 36° equals 360°, or in other words the dust count for the entire spot. If the konimeter samples exactly 10 ml. of air per stroke, then it is unnecessary to multiply by the factor 10 in order to obtain the number of dust particles per ml., as the tens cancel out. The following formula can be used to calculate the number of particles per ml.

$$\frac{\text{No. particles in four } 9^\circ \text{ sectors, or } 36^\circ \times 10}{\text{Ml. sampled per konimeter stroke}} = \text{No. particles per ml.}$$

If 18° sectors are used, generally two sectors are counted and the calculations are made as above. For more accurate work four 18° sectors are counted, but in this instance the factor 10 must be replaced by 5.

To obtain the number of particles per cubic foot in millions, multiply the result by 28,320 and divide by 1 million.

The konimeter is used widely in several countries of the British Commonwealth, namely, in Canada, the Union of South Africa, and Australia. In these countries, it is common to use heat-resistant glass sampling disks, which can be ignited and acid washed before being counted. Thus, for instance, with mineral oil as the adhesive film, the plate is heated to a dull cherry red in a muffle oven, cooled, washed with a few drops of 50 per cent hydrochloric acid and subsequently with water and alcohol, and warmed to remove the alcohol. The dust sample may then be counted with dark-field illumination and a magnification of 150 diameters. (See also page 146.)

c. Owens Jet Dust Counter Samples

It was pointed out that dust particles impinged on slides with the Owens jet dust counter were examined under an oil-immersion objective. The ribbon of dust produced by this sampling instrument may be located with the aid of a 16-mm. objective and dark-ground illumination. Dark-ground illumination may be readily obtained by inserting a suitable stop under the substage condenser. Counts of the particles are generally made using a $^{1}/_{12}$-inch oil-immersion objective. In order to facilitate counting, the eyepiece is provided with a net-ruled micrometer of 1-mm. squares (Fig. 69). With the aid of this eyepiece micrometer, a count of the number of particles in a strip one square wide is made across the entire record at one or two places and an average is taken. This figure multiplied into a factor, depending on the magnification used, will give the number of dust particles on the record. To determine the factor it is first necessary to ascertain the number of strips in the length of the sample ribbon. This may be done by low magnification. For example, with a $^{2}/_{3}$-inch objective, 50 strips in the length of the ribbon are found. Then, the $^{1}/_{12}$-inch objective, which is found to magnify 10 times as much as the $^{2}/_{3}$-inch objective, will have 500 strips. Assuming that 300 particles are found in a strip across the ribbon using a $^{1}/_{12}$-inch objective and that the volume of air sampled was 50 ml., then the number of particles per ml. will be

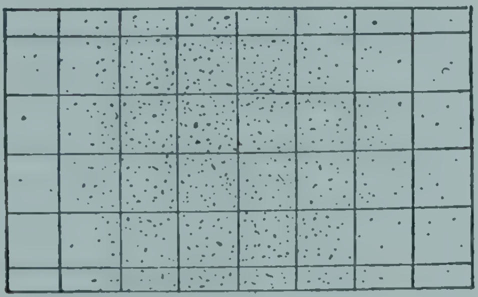

Fig. 69. Typical Owens dust record and ruled ocular disk.[100]

$$\frac{300 \times 500}{50} = 3{,}000$$

If S represents the number of strips found in the record, N the number of particles per strip, and V the number of ml. drawn through the jet in making the record, then

$$\frac{N \times S}{V} = \text{No. particles per ml.}$$

Actually the dust record made by the Owens jet dust counter is not a ribbon of equal width throughout its entire length, for it has knob-like ends. Therefore the count as described above is not exactly correct. Kagan and Broumstein[114] use a graphic method of distribution triangles. For most practical purposes the counting method described above serves adequately.

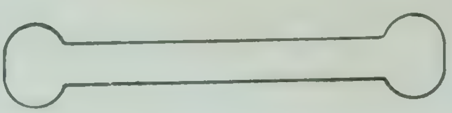

Fig. 70. Shape of Owens dust record (greatly magnified).

d. Electronic Counting

Particles in aerosols may be counted electronically by an experimental device described by Guyton.[115] In this instrument a vacuum sucks the air through a jet at high speed so that particles in the air stream are impacted against a wire or metal plate. The impact of impingement produces an electrical impulse that can be amplified and recorded either on a counter or an oscilloscope. This electrical pulse appears to be generated electrostatically between the particle and the pickup wire or between the particle and the turbulent air in the nozzle. With a jet aperture of 0.8 mm. in diameter, a jet taper of 45°, and a wire 0.4 mm. in diameter almost in contact with the orifice, 61 per cent of the particles are counted. There is no additional change in air flow when the pressure difference between the two ends of the pickup is increased beyond the critical value of 36 cm. of Hg. By holding the vacuum line pressure below the critical value, equivalent to a critical flow of 5.75 liters per minute, it is not necessary to record the flow. The air flows from the jet at about 345 meters per second, approximately the speed of sound.

When a metal plate is used it is held at 1 mm. from the opening of the jet. With the plate all particles above a certain size are counted. The pulse duration is a limiting factor in the efficiency of the device. Water particles do not record readily unless the pickup wire is charged. The particle size recorded is of the order of 2.5 μ and above, but smaller particles may be counted by altering the design of the machine. The device may possibly be constructed to count concentrations of particles from a few particles to several million per liter.

e. Gold-Leaf Dust Indicator

The gold-leaf electroscope dust indicator is based on the principle that dust can be charged electrically by means of an electrified plate. The air stream carrying the charged dust particles is drawn through an electroscope, the rate of discharge being proportional to the number of dust particles. Thus the number of dust particles can be estimated from the time necessary to collapse the leaves of the electroscope.

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[114] M. Kagan and W. Broumstein, *J. Ind. Hyg.*, *13*, 10 (1931).
[115] A. C. Guyton, *J. Ind. Hyg. Toxicol.*, *28*, 133 (1946).

2. *Measurement of Size of Dust Particles*

Because dust particles have, in general, been crushed or ground, they seldom have definite geometrical shape. Therefore they really do not have what is commonly understood to be a diameter. By an arbitrary convention, the "size" of a dust particle is assumed to be the distance between the extreme points of a dust particle when measured in a horizontal direction.[116]

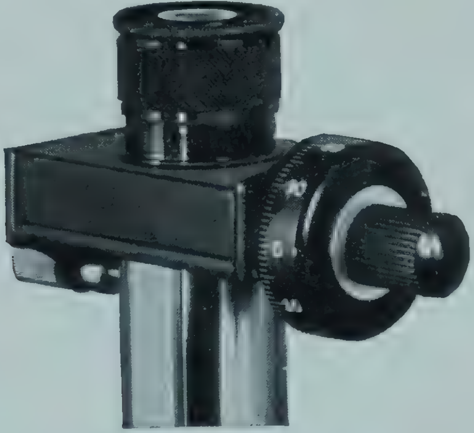

Fig. 71. Filar micrometer eyepiece.
(*Courtesy Will Corporation*)

The Owens jet dust counter and filter-paper methods are used extensively as the sampling instruments for the measurement of the size of dust particles because they obtain samples of dust from an atmosphere in a more or less unaltered condition. The Greenburg-Smith impinger samples may also be used for this purpose; however, some question exists as to the shattering of particles in this method of sampling.[117-119]

Measurements of the size of particles can be made by means of a filar micrometer ocular, using an oil-immersion objective with a magnification of 1.000 diameters. With this magnification particles as small as 0.5 μ can be measured, while smaller particles can be distinguished and recorded. The filar micrometer eyepiece is calibrated so that one division on the micrometer represents a known length on the stage of the microscope. After the microscope is focused upon a representative section of the sample, the horizontal diameters of 200 particles are measured with the

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[116] P. Drinker and T. Hatch, *Industrial Dust*, McGraw-Hill, New York, 1936.
[117] J. B. Ficklen and L. L. Goolden, *Science, 85,* 587 (1937).
[118] E. L. Anderson, *J. Ind. Hyg. Toxicol., 21,* 39 (1939).
[119] L. Silverman and W. Franklin, *J. Ind. Hyg. Toxicol., 24* 80 (1942).

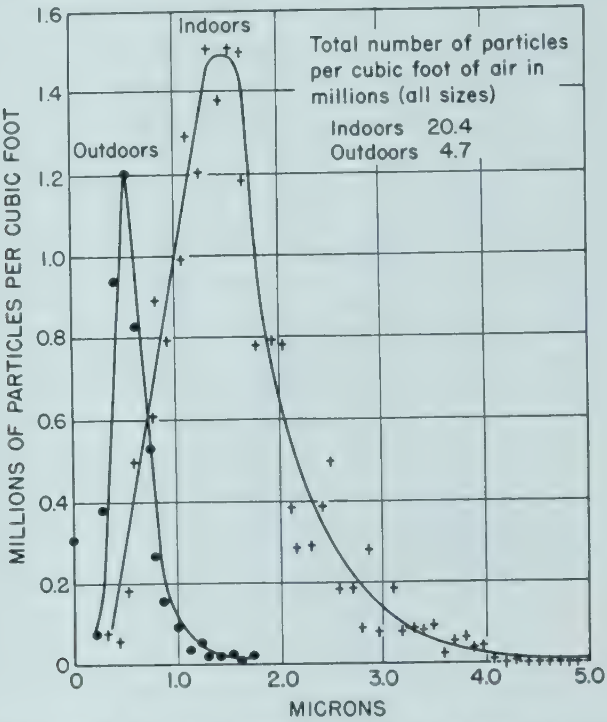

Fig. 72. Amount of dust of different sizes found in the general atmosphere of granite-cutting plants in comparison with that outdoors in the vicinity of these plants.[121]

filar micrometer, moving the cross-hair across the field from left to right and measuring the first 200 particles encountered. This is done in several representative fields. The sizes of the particles are recorded in terms of divisions of the filar micrometer and may later be converted into μ (or microns) by means of a calibration factor. Only one dimension of the particles need be measured, since the particles lie in the field at random and it is impossible to rotate the stage of the microscope, at times. Because, however, a large number of particles can be measured, if desired, the results are the same as if the average of the length and breadth are determined for each particle.

By means of a filargraph,[120] the measurement of particle size can be

[120] E. D. Palmes, *J. Ind. Hyg. Toxicol.*, *26*, 64 (1944).

[121] J. J. Bloomfield, *U. S. Pub. Health Repts.*, *48*, 961 (1933).

made mechanically and a permanent inked record permits simple particle-size grouping.

The size of dust particles may also be obtained by the use of photomicrographs. In order to obtain good results the particles must be in one plane, have no Brownian movement, and be well dispersed. Since industrial dusts are seldom uniform in size, the first requirement cannot be filled. Bloomfield and DallaValle hold that there is not much to be gained by use of photomicrographs over the simpler and less expensive filar-micrometer method. There is unquestionably a more permanent record obtained by the use of the photographic method and there is the further advantage that it is less strenuous and less fatiguing to the analyst.

a. Size Frequency

The frequency with which any particle size occurs is, obviously, the number of times that a particular particle size occurs in a given count.

TABLE 6

Size-Frequency Distribution of Various Industrial Dusts as Compared to Outdoor Dust[121]

Kind of dust	Number of samples	Median	Average frequency in per cent—Size group in microns											
			0 to 0.49	0.5 to 0.99	1.0 to 1.49	1.5 to 1.99	2.0 to 2.49	2.5 to 2.99	3.0 to 3.49	3.5 to 3.99	4.0 to 4.49	4.5 to 4.99	5.0 to 5.49	5.5 to 5.99
Outdoor dust	179	0.5	56.0	41.0	2.5	0.5	—	—	—	—	—	—	—	—
Sandblasting	9	1.4	1.4	19.7	34.7	20.3	12.6	5.2	2.8	1.6	1.1	0 2	0.2	0.2
Granite cutting	4	1.4	2.0	19.0	33.6	24.5	10.4	4.6	3.1	0.6	0.9	0.3	1.0	—
Traprock milling:														
Crusher house	1	1.4	0	13.0	39.0	33.0	10.5	2.5	2.0	—	—	—	—	—
Screen house	1	1.3	2.0	31.5	33.0	16.0	10.0	4.5	2.5	0.5	—	—	—	—
Disk crusher	1	0.9	10.0	48.0	31.0	6.0	3.0	1.0	1.0	—	—	—	—	—
Foundry parting compound	2	1.4	0.5	22.0	42.0	17.3	9.2	5.0	1.5	2.0	0.5	—	—	—
General foundry air	1	1.2	0	26.0	48.0	17.0	8.0	1.0	—	—	—	—	—	—
Talc milling	1	1.5	0	16.0	32.0	20.0	13.0	7.0	5.0	2.0	2.0	2.0	0	1.0
Slate milling	1	1.7	1.0	13.0	29.0	17.0	14.0	14.0	6.0	4.0	1.0	0	1.0	—
Marble cutting	1	1.5	0	12.0	37.0	21.0	10.0	11.0	3.0	0	1.0	2.0	2.0	1.0
Soapstone dust	2	2.4	1.2	16.0	19.0	13.0	11.0	6.0	6.5	4.5	5.5	3.3	2.5	11.5
Aluminum dust	1	2.2	3.0	8.0	20.5	14.0	11.5	9.0	6.5	3.0	3.5	4.0	7.0	10.0
Bronze dust	1	1.5	1.0	12.0	33.5	25.0	21.0	6.0	1.5	—	—	—	—	—

This can be expressed as a per cent, if that number is divided by the total number of particles measured. Such frequencies can be studied either graphically or tabularly, as shown in Figure 72 and in Table 6. Thus percentage number can be plotted against size.

The importance of size frequency can be gleaned from the fact that many investigators have shown that most of the dust particles recovered from both human and experimental animal silicotic lungs were between 1 and 3 μ in size. It has already been pointed out that the significant sizes of hazardous industrial dusts fall within the range of 0.5 to 10 μ.[121]

b. Microprojector

A microprojector for the determination of particle-size distribution and number concentration of atmospheric dust is described by Brown and Yant.[122-124] The theory and practice of microprojection are described in detail in a number of texts.[125-127] This procedure has been used and found to be satisfactory for measuring the particle-size distribution of sub-sieve-size substances, such as pigments and powders,[128,129] which are of the same size range as atmospheric dust. The U. S. Bureau of Mines has used the microprojector and found it to be satisfactory for (1) the determination of the number concentration of atmospheric dust in samples collected by the Owens jet dust counter; (2) particle-size distribution in samples of atmospheric dust collected by the Owens jet dust counter and by the electric precipitator; (3) particle-size distribution of dusts, blood cells, bacteria, and pollen; and (4) it may also be used for counting impinger samples.

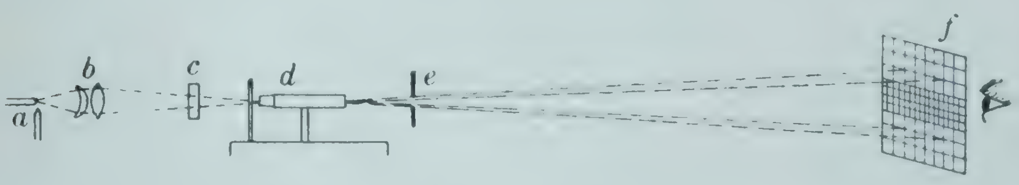

Fig. 73. Microprojector.[122]

The microprojector used by the U. S. Bureau of Mines is shown diagrammatically in Figure 73. It consists of an arc lamp (*a*); a condensing lens (*b*) for concentrating the light from the arc lamp; a water cell (*c*) for filtering heat from the light before it enters the microscope (*d*);

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[122] C. E. Brown and W. P. Yant, *U. S. Bur. Mines, Rept. Invest. 3289* (1935).
[123] C. E. Brown, L. A. H. Baum, W. P. Yant, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3373* (1938).
[124] C. E. Brown and H. H. Schrenk, *U. S. Bur. Mines, Inform. Circ. 7026* (1938).
[125] E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Wiley, New York, 1938.
[126] S. H. Gage and H. P. Gage, *Optic Projection*, Comstock, Ithaca, 1914.
[127] P. Drinker, R. M. Thomson, and J. L. Finn, *J. Ind. Hyg.*, *7*, 567 (1925).
[128] E. J. Dunn, *Ind. Eng. Chem., Anal. Ed.*, *2*, 59 (1930).
[129] *Proc. Am. Soc. Testing Materials*, *30*, Part 1, 919 (1930).

a light shield (e) for shutting off all light except that which strikes the screen; and a screen (f) onto which the images are projected. The screen, which is 50 cm. square, consists of a piece of ordinary blue tracing cloth lacquered on both sides and ruled into centimeter squares. The horizontal 10-cm. strip across the center of the screen is ruled further into $^1/_2$-cm. squares. Most observations are made in this strip. From a position in back of the screen the observer can examine the images directly in front of him without casting shadows on the screen. Remote controls are necessary to permit the observer at the screen to focus the microscope and to operate the mechanical stage. Microprojectors are commercially available.

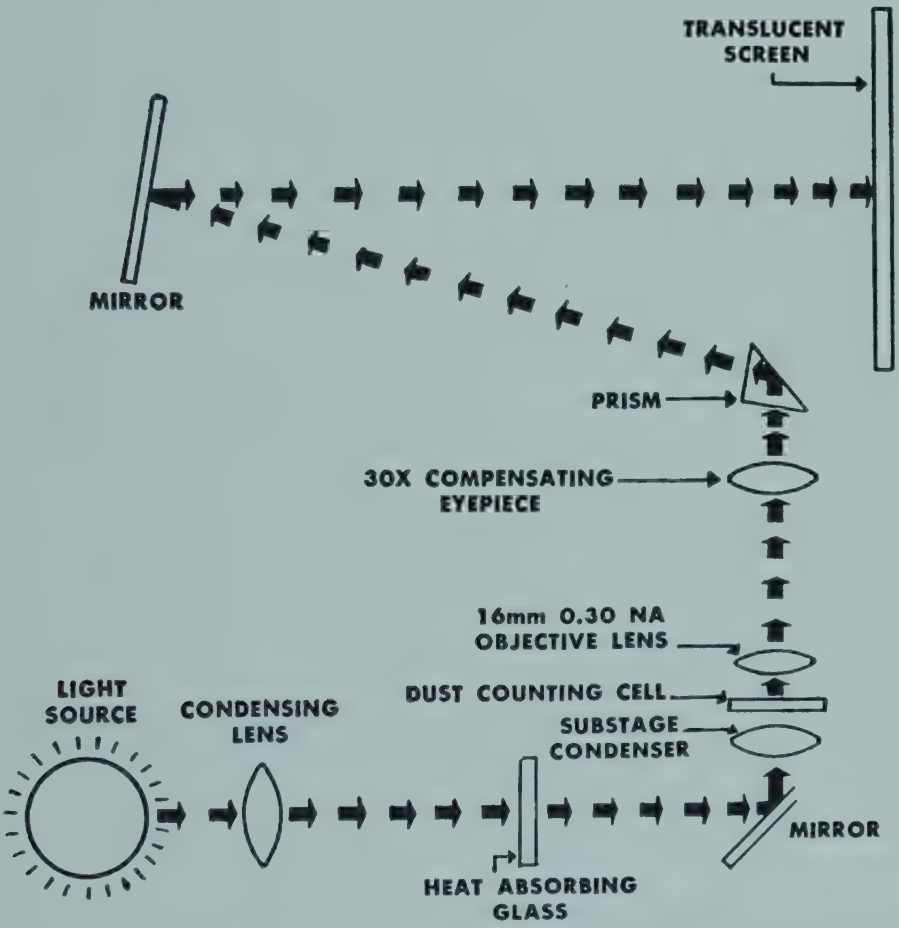
TRANSLUCENT SCREEN
MIRROR
PRISM
30X COMPENSATING EYEPIECE
16mm 0.30 NA OBJECTIVE LENS
DUST COUNTING CELL
SUBSTAGE CONDENSER
LIGHT SOURCE
CONDENSING LENS
MIRROR
HEAT ABSORBING GLASS

Fig. 73A. Schematic diagram of Dust-Vue microprojector. (*Courtesy Mine Safety Appliances Co.*)

Particle-size distribution is determined by comparing the size of the images with that of the ruled or known areas on the screen.[130] Number concentration of uniformly distributed samples of dust from measured volumes of air is determined by counting the number of particles in known areas. The two determinations usually are made simultaneously on such samples, since the estimation of size involves counting the number of particles. The dust images on the screen are magnified 10,000 diameters.

3. *Gravimetric Dust Analysis*

The gravimetric method of dust analysis has been described in some detail with respect to the thimble-filtration method. Other filtration methods of a similar type lend themselves to the same method of estimation. Dust samples obtained by the sugar-tube method, or an absorption method such as the Greenburg-Smith impinger, can also be estimated gravimetrically. The weight of the dust sampled by the impinger may be determined by evaporating an aliquot of the mixture prepared for the microscope count in a tared dish. The dish is then dried in a constant temperature oven at 100–105° C., placed in a desiccator, allowed to cool, and weighed. The gain in weight is considered the weight of the dust. This is corrected by running a control on the water used, in a similar dish and through the same treatment for the same length of time.

Alternatively a Gooch crucible, prepared with a mat of asbestos sufficiently thick to retain all the dust, may be used. An aliquot of the prepared sample solution mixture is filtered through the Gooch crucible. which is placed in an oven at 105° C. for 4 hours, removed to a desiccator to cool, and weighed.

Total combustible matter can be obtained in both instances, provided the dish is of heat-resistant material, by igniting the dish or crucible, cooling, and weighing. The loss in weight is generally considered organic material. The residue is considered the inorganic portion of the dust.

Methods for the gravimetric estimation of sootfall have been detailed on page 112, *et seq.*

4. *Light Transmission*

The amount of light transmitted through a gaseous or liquid medium containing dispersed opaque particulate matter may be expected to follow the Beer-Lambert law.[131] Various photoelectric instruments have been devised for such measurements, particularly for testing air filters[132] and as smoke detectors.[133–135] Such methods have also been used for estimating the amount of dust.[136–138]

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[130] H. L. Green, *J. Ind. Hyg.*, *16*, 29 (1934).

[131] A. W. Simon, L. C. Kron, C. H. Watson, and H. Raymond, *Rev. Sci. Instruments*, *2*, 67 (1931).

Brown[139] applied such methods to the preliminary estimation of the amount of dust collected by the filter-paper method. The light-transmission equipment consisted of a light source like a flash light, a glass window for the paper holder, and a light meter. The light transmission is measured before and after sampling the dust. A calibration curve can be prepared and the amount of dust may be calculated.

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[132] F. B. Rowley and R. C. Jordan, *Heating, Piping, Air Conditioning, 15,* 487 (1943).

[133] S. R. Reynolds, *Elec. J., 23,* 135 (1926).

[134] F. Sawford, *Mech. Eng., 49,* 999 (1927).

[135] A. S. G. Hill, *Trans. Faraday Soc., 32,* 1125 (1936).

[136] J. F. Cadden and E. T. Roetman, *West Virginia State Dept. Health, Bur. Ind. Hyg. Rept.* (1939).

[137] D. H. Davis and G. R. Gardner, *Trans. Am. Inst. Mining Met. Eng., 149,* 193 (1942).

[138] C. L. Pool, J. Wuraftic, and R. J. Kelly, *Ind. Med., Ind. Hyg. Section 2,* 39 (1941).

[139] C. E. Brown, *U. S. Bur. Mines, Rept. Invest. 3788* (1944).

CHAPTER VI

The Chemical and Microscopic Estimation of Silica

Previous sections have stressed the importance of dusts containing silica as the cause of fibrosis of the lungs. This has been shown to be the cause by many investigators. While most authorities agree that silicosis is a disease caused by breathing air containing free silica, characterized anatomically by generalized fibrotic changes,[1] other investigators point out that some silicates were as likely to cause silicosis[2,3] as free silica. They have isolated the mineral sericite (muscovite), a hydrated potassium aluminum silicate, from silicotic lungs. These investigators contend that certain mineral silicates are as soluble in the lungs as free silica minerals.[4]

Silica is the name given to the chemical compound silicon dioxide, SiO_2. Its most common natural pure crystalline form is quartz. Its most common form, not necessarily pure, is sand, which is quartz that has been crushed by the movement of water. Quartz itself occurs in different crystalline forms, such as tridymite and crystobalite, each of which has a number of crystalline forms. In comparison with quartz, the other crystalline forms of silica are rare.

Silica also occurs naturally in amorphous forms, among the more important of which are chalcedony, carnelian, chrysoprase, and onyx. These forms also are rare in comparison with quartz and seldom, if ever, become an industrial hazard.

1. Nomenclature

In many types of chemical analysis, it is customary to obtain a measure of the silicon present by estimating total silica. This type of analysis, however, fails to distinguish between silicates, on the one hand, and free silica, on the other.

A long-established convention has led to the reporting of chemical analyses of rocks and minerals in terms of certain chemical compounds, as, for example, oxides, rather than in terms of chemical elements. This convention has arisen because in many instances, such as silicon, no purpose would be served by isolating the element itself. Hence the analysis is reported in the form that it is made. For instance, the chemical analysis of an average granite is reported as containing 70 per cent of silica. About 30 per cent, or roughly one-third, of this granite consists of quartz, whereas the other two-thirds of the granite is made up chiefly of minerals that are complex salts of silicon-bearing acids. These acids are known as silicic acids, and the salts of these acids are termed silicates. The remainder of the material reported as silica in this analysis comes from the silicate minerals of the granite, chiefly feldspar and mica.

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[1] R. R. Sayers and R. R. Jones, *U. S. Pub. Health Repts., 53,* 1453 (1938).
[2] W. Jones, *J. Chem. Met. Mining Soc. S. Africa, 34,* 99 (1933).
[3] J. W. Matthews, *Analyst, 63,* 467 (1938).
W. Jones, *Analyst, 59,* 456 (1934).

This system of reporting rock and mineral analyses, as well as other analyses, in terms of oxides necessitates the use of the expressions *free silica* and *combined silica* to distinguish between the silica that makes up quartz or the other forms of minerals composed of silica alone, and the silica that is combined with other elements in the various silicate minerals. Thus in the afore-mentioned sample of granite which contained 70 per cent silica, the total silica is composed of 30 per cent free silica plus 40 per cent combined silica. Quartz and other forms of the chemical compound SiO_2 are termed *free silica,* that contained in feldspar and other silicates is known as *combined silica.*

As the relative danger of silicosis[5] to workers in certain dusty trades—among which may be mentioned rock drilling, granite cutting, foundries, and the manufacture of scouring powder—is determined chiefly by the amount of free silica present in the dust in the form of quartz rather than by the silica that is in chemical combination, it is necessary to use a method which will enable one to estimate how much of the dust of a given sample consists of quartz.

2. *Free-Silica Standards*

The dust hazard is regulated in certain states by code. These permissible dust concentrations are tabulated in Table 7, Appendix. Thus in New York State it is regulated, in so far as rock drilling is concerned, by Industrial Code No. 33 and certain rules promulgated by the Industrial Commissioner. According to the terms of this Code, all rock formations are divided into two classes depending on their free-silica content, as follows:

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[5] A. Knopf, *U. S. Pub. Health Repts., 48,* 183 (1933).

Class 1—rock formations containing uniformly less than 10 per cent by weight of free silica.

Class 2—rock formations containing 10 per cent or more by weight of free silica and those formations having variable and unpredictable content of free silica.

Under this classification the Code allows dust concentrations up to and including 100 million particles per cubic foot of air for drilling operations in Class 1 rock, whereas the maximum permissible dust concentration for drilling in Class 2 is fixed at 10 million particles per cubic foot of air. It is clear that in the enforcement of such a Code, the problem of determining a just classification of rock is very important.

3. *Sampling in Quarries*[6]

Some quarries are many acres in area and have working faces as high as 200 feet. Often there are several formations of different kinds of rock occurring at various depths or at different sections of the quarry. A representative sample cannot be obtained under such conditions merely by sampling the rock at one point. Therefore, in order to obtain samples that are representative of the quarry as a whole, the specimens should be taken from the large storage piles of quarried stone that has been through the crushing process. These piles often represent the accumulation of several months of operation and contain well-mixed stone from all parts of the quarry. Sampling of these piles may be done with the aid of a clam-shell bucket or bucket loader. Take grab samples here and there from the pile and from its interior with the bucket and deposit these grab samples together in a separate pile. After a representative sample has been taken, it should be thoroughly mixed by raising and dropping the stone by means of the bucket. Because the sample pile taken in the manner described usually amounts to from 1 to 2 tons, it is necessary to quarter it until a final sample of about 35 pounds is obtained.

In a few of the largest crushed-stone quarries the sampling procedure is considerably simplified because the crushed stone is stored in large concrete silos that are filled and unloaded via a conveyor system. Here conveyor belts lead from under the bins to the wharfage or railroad siding, where scows or freight cars receive the stone for shipping. To obtain a good sample of the quarry's production here, it is only necessary to open the discharge gate in the storage bin selected and run about a ton of stone onto the conveyor. Handfuls or scoopfuls of rock can then be selected at random from the belt until a 35-pound composite sample is obtained.

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[6] L. Greenburg, C. B. Ford, W. J. Burke, and B. H. Dolin. *N. Y. State Ind. Bull.*, 17, 575 (1938).

4. Petrographic Analysis[7,8]

The methods for the estimation of free silica in a dust fall into three main groups of analysis, namely, petrographic, chemical, and physical-chemical methods such as spectrographic and x-ray analysis.

A petrographic analysis is one in which the identity of a material is established by a study of its structure, texture, color, refractive index, and other optical properties and the like. In the case of rock analysis, this can be done with the aid of a petrographic or polarizing microscope. This type of microscope has in addition to its usual equipment three other pieces of apparatus. It needs a polarizer or a Nicol prism in order to polarize the light; an analyzer, which is another prism needed to examine the light after it has passed through the polarizer and the thin section of rock which is being examined; and a rotating stage, which revolves about an axis in the line of sight of the microscope. A petrographic microscope has been described by Faust.[9]

In the petrographic method a thin section or rock specimen is examined. Therefore, it cannot be used, as such, on collected dust. However, if some of the material with which or upon which a worker works is available, then the petrographic method may be applied to that. A section approximately 0.03 mm. thick should be cut from the material to be examined. This is mounted in Canada balsam on a glass slide. Powdered specimens may also be examined in this way, but the grains of powder must be about 0.06 mm. in size. Particles less than 10 μ in size cannot be accurately identified with a polarizing microscope. Various oils are used in which to immerse the grains, depending upon their refractive indices. By means of the Rosiwal method a quantitative estimate of the amount of quartz in a mineral can be made. This is done by measuring the linear intercepts of a given mineral along numerous parallel lines, the percentage of quartz being determined by the ratio between the sum of all of the intercepts of quartz and the length of the measured traverse. It can be shown mathematically that the linear inter-

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[7] H. L. Ross and F. W. Sehl, *Ind. Eng. Chem., Anal. Ed.*, 7, 30 (1935).

[8] G. T. Faust and A. Gabriel, *U. S. Bur. Mines, Inform. Circ. 7129* (1940).

[9] G. T. Faust, *U. S. Bur. Mines, Rept. Invest. 3503* (1940).

cepts are proportional to volumes. The measurement is carried out by the use of a screw-micrometer ocular or a mechanical stage.

a. Petrographic Estimation of Quartz in Atmospheric Dust

The percentage of quartz and material having approximately the same refractive index as quartz in a specimen of dust whose origin is not definitely known, as, for instance, open-air dust,[10] may be determined by immersing a specimen in an oil of known refractive index and observing the sample under dark-field illumination. When the source of the dust is known, as, for instance, in samples taken in a tunnel or mine, then oils of various refractive indices are used.

Atmospheric dust samples may be collected by the methods detailed in the previous chapter. Those that are collected on micro cover glasses may be used directly; those collected on celluloid or metal foil, as in the case of the electric precipitator, should be transferred by scraping off a representative sample of the dust and placing it on a microscope slide; those collected by the impinger, using alcohol as the collection medium, are centrifuged in order to tranfer the dust to a micro slide.

Preparation of Sample. Support a dark-field type, No. 1 thickness, 9-mm.-diameter cover slide in a glass tube 17 mm. in diameter and 12 cm. long so that it rests flat on a bottom stopper. Add a 5-ml. aliquot of a well-shaken dust sample from the impinger, stopper the upper end of the tube, and centrifuge at 3,000 to 3,500 r. p. m. for 15 minutes. Remove the top stopper, loosen the bottom stopper so that the alcohol can drain away, and slowly turn the tube to a horizontal position by the time all of the alcohol has drained off. Remove the bottom stopper, holding it so that the cover slide is in a vertical position held in place by the alcohol. This action assists in complete drainage of the alcohol. Remove the cover slide from the stopper with a forceps, place on filter paper to dry, and then place in an inverted position on a slide for examination.

Procedure. Set a microscope for dark-field illumination. Run a drop of a mixture of mineral oil and α-chloronaphthalene with an index of refraction of 1.56 around the dust sample, between the cover glass and the slide. Another mixture that may be used is mineral oil and α-bromonaphthalene. The liquids like xylidine, bromobenzene, and tri-*o*-cresyl phosphate, which also have a refractive index in the neighborhood of 1.56, may also be used. Estimate the percentage of quartz and minerals with a similar refractive index to the nearest 10 per cent by number, basing this estimate on the factors that quartz and the minerals of similar refractive index appear as faint blue to gray particles without a halo, while transparent particles of different indices show brighter colors with a halo, and opaque particles show a peculiar shade of bright orange. Since the density of quartz is 2.65 and the density of most of the common minerals ranges from 2.5 to 3.0, the value obtained may be accepted as the percentage by weight.

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[10] W. D. Foster and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3368* (1938).

As Foster and Schrenk note, this method fails to distinguish between quartz particles and those of similar refractive index. Any mineral with an index in the range 1.53 to 1.59 may be confused with quartz; for this reason the material identified as quartz by this method may be quartz, may be a mixture of quartz and other minerals, or may actually contain no quartz at all. However, in practical work, the feldspars will be the ones usually found. Other common minerals which it may not be possible to distinguish from quartz by the procedure outlined are anhydrite, chlorite, halite, kaolinite, some of the micas, serpentine, and talc. While Larsen and Berman[11] list some 240 minerals with the intermediate refractive index (beta) in the range 1.53 to 1.59, the majority of the minerals with refractive indices similar to that of quartz are rare so that significant amounts will ordinarily not be found in dust. Thus, though this method does not identify quartz as such in a dust, it is useful in setting a maximum limit for the amount of quartz possibly present, giving, in effect, high values but not low values for the quartz content. If no quartz is found by the procedure detailed above, less than 1 per cent of quartz is present.

The method may be modified to make estimates of quartz in dusts whose approximate composition is known by immersing samples of the dust under separate cover glasses in oils of different refractive indices, such as 1.53, 1.545, 1.56, and 1.70, and noting the disappearance of certain particles. Thus quartz will apparently disappear in an oil with a refractive index of 1.545, albite will apparently disappear in an oil with a refractive index of 1.53, hornblende and pyroxene appear faint in an oil of refractive index of 1.70, and analogous conditions can be arranged for other minerals.

b. Modified Petrographic Immersion Method

Ross and Sehl[12] have modified the petrographic method. In their modified petrographic immersion method, separate mounts of powdered mineral or dust are made with fennel-seed oil and mononitrobenzene and then are examined with an ordinary microscope equipped with a Whipple disk (Fig. 65). The method depends on the principle, known as the method of central illumination,[13,14] in which a nonopaque body or material is identified by its optical behavior in an immersion medium having an index of refraction different from the material being examined.

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[11] E. S. Larsen and H. Berman, *U. S. Geol. Surv., Bull. 848* (1934).

[12] H. L. Ross and F. W. Sehl, *Ind. Eng. Chem., Anal. Ed.*, 7, 30 (1935).

The quartz or free silica commonly encountered has a definite index of refraction, namely, 1.544. Certain minerals have higher and others have lower indices of refraction. If dust, consisting of quartz and minerals of lower and higher refractive indices than quartz, is immersed in fennel-seed oil, which has a refractive index of 1.540, a microscope objective focused correctly and then raised above this point of good focus makes several particles appear lighter than the surrounding medium while the remainder appear darker. The bright or transparent particles will consist of quartz plus particles which have a higher refractive index than quartz. Similarly, if another portion of the same dust is immersed in mononitrobenzene, which has a refractive index of 1.55, some of the particles appear brighter than the surrounding medium when we raise the objective slightly above the point of good focus. In this instance, however, the bright or transparent particles are only those which have a higher refractive index than quartz. Therefore, if the percentage of transparent particles in the fennel-seed oil is placed equal to A and the percentage of transparent particles in mononitrobenzene is placed equal to B, then

$$A - B = \text{per cent quartz or free silica}$$

Preparation of Sample. Care should be exercised in the selection and preparation of the sample. Only a very small amount of powder need be examined. It should be uniform and representative. Rock specimens are crushed, quartered, and ground in an agate mortar to pass a 150-mesh screen. Samples of dust taken from rafters, beams, ledges, and the like need not, in general, be ground, for they are usually of the correct size.

Preparation of Slides. Place a very small amount of ground mineral or dust, approximately 10 mg., in a 50-ml. beaker, add 5 ml. of fennel-seed oil, and swirl so as to obtain a suspension of the mineral particles in the oil. Make a similar suspension of the ground mineral or dust in mononitrobenzene. Use a pipette or a medicine dropper to transfer a

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[13] E. S. Larsen and H. Berman, *U. S. Geol. Surv. Bull. 848* (1934).

[14] E. S. Larsen, *U. S. Geol. Surv. Bull. 679* (1921).

sufficient amount of oil-mineral suspension to a Sedgwick-Rafter cell. A cover slip, similar to that used in counting dust particles (as explained in Chapter V), should be employed to cover the cell. Thus two slides are prepared, one containing the pulverized mineral or dust specimen in fennel-seed oil, and the other, a similar sample, in mononitrobenzene. The oil should be the purest obtainable. The mononitrobenzene should be redistilled. A new sample of oil should be checked with a pure, ground-quartz specimen to verify the refractive index of the oil. Sunlight affects mononitrobenzene and it should therefore be protected against direct rays of light.

In order to prevent errors, it is good practice to use separate beakers, pipettes, and cells for fennel-seed oil and for mononitrobenzene.

Apparatus. An ordinary microscope, meeting the U. S. Public Health Service specifications, as described in Chapter V, page 145, may be used for this method. Ross and Sehl used a microscope with a 7.5× eyepiece and a 16-mm. objective. They suggest a higher powered microscope for very fine dusts. The eyepiece, as explained, must be provided with a Whipple disk (Fig. 65). As a means of illumination, an ordinary small electric microscope lamp is used.

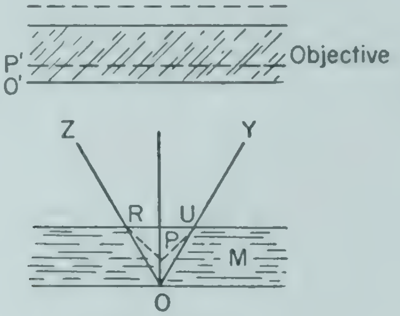

Figure 74.[12]

Method. After the Sedgwick-Rafter cell has been filled and a cover slip placed over it, having been exercised to exclude all air bubbles, it is permitted to stand for 30 minutes to allow the dust to settle. After this time has elapsed, place the cell under the microscope and raise or lower the objective until a point is reached where the dust particles are visible. It is not necessary to focus through the entire depth of the liquid, because nearly all the particles will have settled to almost a single plane within the 30 minutes. A sufficient amount of sample should be taken to show about 2,000 particles on the entire Whipple disk field.

In Figure 74, *O* represents the definite position of the objective in the case of a particle in focus when nothing but air separates the particle from the objective. If a transparent plate M of any medium is placed over the particle, between it and the objective, it is necessary to raise the objective somewhat to bring the object back into focus. This is due to the fact that all rays from O are refracted away from the normal on emerging from the transparent plate, as illustrated in Figure 74 by the two rays ORZ and OUY. In order to bring the particle back into focus, it will then be necessary to raise the objective through the distance OP or $O'P'$.

Since nearly all the particles of minerals or dusts are thinner on the edge than in the center, when they are immersed in liquids they act as imperfect lenses to refract the light, provided they differ in index of refraction from the liquid. If the particle has a higher index than the liquid, it tends to bring light to the focus above the fragment. Therefore, a slight raising of the objective from good focus on the particle causes brightness or transparency within the area of the particle. As the microscope tube is raised higher above focus, this bright area contracts and becomes brighter or more transparent. If the tube is lowered below focus, the particle appears darker than the rest of the field and a highly illuminated halo may surround it. As the tube is lowered, this halo moves outward from the particle. If the mineral has a lower index of refraction than the liquid, it brings light to a focus before the particle. Therefore, a slight lowering of the objective from good focus on the particle causes brightness or transparency within the fragment, and conversely a slight raising above good focus causes the particle to darken.

In order to obtain quantitative results, it is necessary not only to count the number of particles but to apportion to each particle its due weight, depending upon its size. Ross and Sehl divided the particles into two unit sizes, the first including those particles having an area of less than one-tenth the area of the smallest division on the Whipple disk. These units are given a weight of 1. The second grouping includes all the larger particles, which are divided into 10-units, each 10-unit being given a weight of 10. A particle having an area of one-tenth of the smallest division on the Whipple disk is called one 10-unit. The entire area of the smallest division on the Whipple disk is given a weight of 100, or ten 10-units. A particle having one-half the area of the smallest square on the disk is given a weight of 50, or five 10-units. It is simpler and more rapid if the larger particles are counted first in units of ten, then the 1-unit particles are counted. The weight of transparent particles may be computed in the following manner:

No. of transparent 10-size units × 10 = A
No. of transparent 1-size particles × 1 = B
$A + B$ = weight of transparent particles

The objective is then lowered until all the particles are in good focus and the procedure outlined above is followed, this time counting and weighting all particles, both light and dark, in order to determine the particle weight.

Total No. of 10-size units × 10 = C
Total No. of 1-size particles × 1 = D
$C + D$ = total weight of all particles

Then

$$\frac{A + B}{C + D} = \text{per cent of transparent particles}$$

This procedure is followed with both the fennel-seed oil cell and the mononitrobenzene cell. In fennel-seed oil, the transparent particles represent quartz and also those minerals having a higher index of refraction than quartz. The transparent particles in mononitrobenzene represent only minerals having a higher index of refraction than quartz. It is clear then that:

per cent of transparent particles in fennel-seed oil minus per cent of transparent particles in mononitrobenzene equals per cent of free silica.

A modified petrographic method to obtain the silica content of dust is used by Franks and Tressidder.[15] Samples obtained by the use of the Kotzé konimeter are used. The glass plate containing the samples is treated with hydrogen chloride vapor and heat. This treatment removes all but the siliceous material from the dust spots. They are then examined with a dark-field microscope. The size, nature, and quantity of the siliceous material affect the quantity of light given off with a dark-field microscope. They found a rough parallelism between the photometric value and the silica content of the dust spots.

While the petrographic method is preferable when the amount of quartz is to be compared with the amounts of such materials as pumice, shale, clay, etc., it is insufficiently quantitative nor can it be applied to fine dust particles. It is very useful as a guide along with the chemical analysis. The Ross and Sehl method, while rapid and of undoubted value, does not attempt to distinguish the other materials present. It has the error of including other minerals whose refractive indices fall between 1.54 and 1.55, although these are seldom present. It is, furthermore, only reasonably accurate.

[15] W. R. Franks and L. C. Tressidder, *Mining Mag.*, *51*, 265 (1934).

5. *Fusion Method*

Quartz is relatively refractory compared to many of the minerals with which it is associated, for it has a melting point of the order of 1700° C. Based upon this property, McIntyre and Bozsin[16] and Salazar and Silverman[17] have devised methods for its estimation.

In the latter method dust, passed through an impinger section, is heated and fused by passage through the air-acetylene flame of a blast burner. The air-fuel ratio is 8.6:1, corresponding to an air flow of 50.9 l. p. m. and an acetylene flow of 5.9 l. p. m. The heated dust is collected by electrostatic precipitation and is caught in a Vycor crucible, from which it is transferred to a microscope slide and examined under high dry or oil magnification.

Use samples of air-borne dust, or rafter dust, or specimens which have been ground so that particles of the size of 10 μ can be obtained.

Procedure. Weigh 1 to 2 g. of the sample, transfer to a beaker, and add a 0.05 per cent of aqueous solution of Triton K-12 or an analogous wetting agent. Place on a hot plate and add sufficient water to wet the sample completely and remove all air. Add an equal volume of concentrated hydrochloric acid, cover the beaker with a watch glass, and heat to boiling. Cool, dilute with 1 to 3 volumes of water, depending upon whether or not a gel has formed, filter through an ashless filter paper, and wash three times with hot water. Transfer the filter paper and contents to a tared crucible, ignite, cool, and weigh to determine the amount of insoluble material.

Grind the residue again, if necessary, to break up any aggregates and transfer to the flask of the fusion apparatus. Light the main burner and the ring burners, adjusting the flame of the former so that it is long, bright, and yellowish white, and so that there is no appreciable air gap between the small canopy and the top of the steel tube. Adjust the flame gradually by means of the flowmeters until the flows mentioned above are obtained. Move the crucible used to catch the precipitate into place and connect the transformer to a current source. Open one by-pass slowly to avoid overloading the chamber and precipitator, while gradually closing the second by-pass valve. Collect sufficient for several glass slides, disconnect the current, and shut off the air and acetylene. Transfer the treated sample from the crucible to the slides with the aid of a camel's-hair brush or razor blade. Estimate the amount of silica by a direct count of the fused and unfused particles.

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[16] C. H. McIntyre and M. Bozsin, *Ind. Eng. Chem., Anal. Ed., 12,* 326 (1940).

[17] A. Salazar and L. Silverman, *J. Ind. Hyg. Toxicol., 25,* 139 (1943).

Refractory materials—that is, materials having melting points considerably higher than that of quartz, like carborundum, chromite, corundum, diasporite, spinel, and zircon—interfere, since such materials would also give unfused particles. Andalusite, dumortierite, kyanite, mullite, and sillimanite may also interfere.

6. Chemical Methods

The amount of free silica in a material can be obtained by the method of ultimate analysis, that is, an analysis in which every element is determined and its proportion in compounds computed. This method is time consuming, laborious, and of no more value in many instances than the methods of proximate analysis in which a certain type of constituent, as, for instance, total silica, is determined. The chemical methods used for the estimation of free silica in the presence of silicate depend on the greater solubility of silicates in hydrofluosilicic acid or in fluoboric acid as compared with the solubility of quartz in these acids. The essential prerequisite for a reagent that can be used for the determination of free silica in the presence of silicate is that its action on silica be slight and its action on silicates be rapid. Chemical methods are generally used on the rock sample itself, rather than on the dust obtained from that rock.

a. Knopf Hydrofluosilicic Acid Method

The Knopf[18] method is a series of acid digestions in which the carbonates of the dust are decomposed by hydrochloric acid, the silicates are decomposed by cold hydrofluosilicic acid, H_2SiF_6, and the silica is decomposed by hydrofluoric acid, H_2F_2.

Preparation of Sample. If nonpulverized rock is being examined, grind the material to pass a 150-mesh sieve. This treatment will insure a certain uniformity in size and will aid the action of the hydrofluosilicic acid. Dust ordinarily need not be ground.

Procedure. Weigh 0.5 g. of the properly prepared sample into a tared, ignited platinum dish. If the preliminary petrographic examination shows the presence of any organic material, the dish should be placed in a muffle oven at white heat for 30 minutes to burn off the organic matter. Dusts that contain much oil should be defatted with petroleum ether, filtered, and the filter and residue returned to the platinum dish, which should then be ignited as described above. Cool.

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[18] A. Knopf, *U. S. Pub. Health Repts., 48,* 183 (1933).

If the preliminary examination shows the presence of carbonates, add hydrochloric acid to the dish and heat gently. After the action has ceased, filter on ashless filter paper, wash well with water, return the filter and the residue to the platinum dish, dry, and then ignite again. Allow to cool.

Add hydrofluosilicic acid in moderate excess to the residue in the platinum dish. If the composition of the dust shows no carbonates to be present, the hydrochloric acid treatment is not necessary and the hydrofluosilicic acid may be added directly after the sample is weighed, if no organic matter is present, or after the first ignition and cooling, if organic matter is present. Cover the crucible or dish and set it away in a place where the temperature is reasonably constant and not above room temperature. Care must be exercised not to raise the temperature during the hydrofluosilicic acid treatment, because hydrofluosilicic acid decomposes on heating into silicon tetrafluoride, SiF_4 and hydrofluoric acid, H_2F_2. The hydrofluoric acid will, of course, attack any silica that may be present. Permit the dish to remain with the hydrofluosilicic acid acting on the silicates present for 24, 48, or even 72 hours, depending on the amount and difficulty with which the silicates present dissolve.

Decant the contents of the dish carefully onto an ashless filter paper and wash the crucible thoroughly, the washings being passed through the filter paper. Wash the residue until the wash water gives no precipitate in a clear mixture of dilute potassium chloride and 95 per cent alcohol. Return the filter and its residue to the platinum dish or crucible, dry, ignite, cool, and weigh. The loss in weight is noted and is calculated as silicate. The hydrofluosilicic acid treatment is continued until the weight of the residue remains relatively unchanged.

Treat the residue unchanged by the hydrofluosilicic acid with 2 to 3 ml. of 48 per cent hydrofluoric acid. Free silica volatilizes completely with hydrofluoric acid. Repeat the hydrofluoric acid treatment, if necessary. Ignite, cool, and weigh. The loss in weight may be calculated as free silica.

Hydrofluosilicic acid does have some solvent action on free silica even at low temperatures. The more insoluble the silicates present, the greater length of time will be necessary for them to be dissolved and therefore the greater the amount of free silica dissolved also. Knopf[18] has, however, shown that the rate of loss in weight, that is, the rate of solubility of free silica in hydrofluosilicic acid, is relatively constant. Therefore a correction factor or equation can be used to correct for the amount of free silica dissolved by the hydrofluosilicic acid during the time it was in contact with the free silica. This will be shown in a succeeding section. Knopf found an average of 0.7 per cent per day as the rate of loss in original weight of the silica. By using this factor of error, it is possible to compute at the end of an analysis the maximum possible loss in weight of quartz originally present and thus obtain a maximum figure for quartz.

Moke[19–21] found that the action of hydrofluosilicic acid against pure quartz increases with decreasing particle size. Thus the smaller the particles being treated by this method the greater the solubility of silica and therefore the greater the error involved. To minimize this error, grind the rock to pass a 150-mesh sieve but not so fine as to pass a 200-mesh sieve or screen. Analyze only the portion whose particle size falls between 150-mesh to 200-mesh fineness.

b. Fluoboric Acid Method

Line and Aradine[22] point out that there is a comparatively large correction factor to be applied in the Knopf method. They suggest the use of fluoboric acid as the silicate solvent. In their method, the silicates are decomposed by fluoboric acid, which attacks free silica much less than does hydrofluosilicic acid. Thus at room temperature, quartz lost only 0.3 per cent per day in fluoboric acid, as compared to a loss of 0.7 per cent per day for hydrofluosilicic acid, while the silicates generally dissolved more readily in fluoboric than in hydrofluosilicic acid. Moreover, fluoboric acid does not decompose as readily as hydrofluosilicic acid does at higher temperatures, its solvent action is greater, and therefore the time of solution is greatly reduced.

Preparation of Fluoboric Acid. Dissolve 32 g. of purified boric acid in 75 ml. of pure 48 per cent hydrofluoric acid. Pour the hydrofluoric acid into a 125-ml. platinum dish and cool this in an ice bath. Keeping the dish in the ice bath, add the boric acid in small amounts, allowing each portion to dissolve before more is added. In this way the solution does not become overheated. When all the boric acid has been added, even though the last portion added may not dissolve while the solution is cold, concentrate the solution to about 50 ml. on a steam bath. Cool to 0–5° C. and filter. The resulting acid is a slightly yellow, fuming, syrupy liquid that should have a specific gravity of about 1.45 and should

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[19] T. Hatch and C. B. Moke, *J. Ind. Hyg. Toxicol., 18,* 91 (1936).
[20] C. B. Moke, *J. Ind. Hyg. Toxicol., 18,* 299 (1936).
[21] M. W. Travers, *Chemistry & Industry, 58,* 226 (1939).
[22] W. R. Line and P. W. Aradine, *Ind. Eng. Chem., Anal. Ed., 9,* 60 (1937).

analyze about 40 to 45 per cent HBF_4 by the Lange[23] method. It should give no test for fluoride with calcium chloride or lead nitrate solutions. It must be stored in wax or rubber bottles, but the filtration may be made with glass apparatus.

Apparatus. For maintaining the crucibles at a constant temperature for long periods, a large vacuum desiccator may be placed in an electric oven, the heating unit of which is controlled by a thermostat. An outlet tube is connected to a suction pump and a constant current of warm air is drawn through the desiccator to remove the fumes. The inlet tube may be arranged so that a thermometer can be inserted into the desiccator to check the temperature at which the digestion is taking place without disturbing the apparatus.

Procedure. Weigh into a platinum crucible or dish 0.15 to 0.2 g. of the sample that has been ground to pass a 100-mesh sieve. Add 5 ml. of fluoboric acid, 1 ml. of phosphoric acid, sp. gr. 1.39, and 2 ml. of 2 M ferric chloride. Heat the crucible at 50° C. for 48 hours, adding more ferric chloride if the yellow color of the solution fades. Transfer the residue to an ashless filter, wash four times with N hydrochloric acid, and five times with hot water. Unless the residue is negligible at this point, place paper and residue in the crucible and destroy the paper by heating the crucible only to dull redness. Repeat this treatment for 48 hours longer. Filter, wash, and determine the weight of the residue. Unless solution has been complete, repeat this treatment for 48-hour periods until a loss of only 1 to 2 mg. is found. This indicates complete solution of the silicate.

Some siliceous materials may be decomposed in less than 48 hours, in which case the treatment with fluoboric acid should be stopped as soon as complete decomposition is apparent. Experience with known materials and dusts will give this information. In other instances, even 8 or 12 days may not effect complete decomposition.

Treat the residue insoluble in fluoboric acid with 2 to 3 ml. of 48 per cent hydrofluoric acid, and repeat until constant weight is obtained after ignition. The loss in weight corresponds to the free silica content of the residue. This value must be corrected for the amount of free silica dissolved during the time required to decompose the silicate. The correction factor is 0.34 per cent per day.

When the residue is practically pure silica, the treatment with hydrofluoric acid will give the correct value for quartz; if undecomposed silicates remain, the loss with hydrofluoric acid will be too high, owing to attack of the silicates.

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[23] W. Lange, *Ber.*, *59*, 2110 (1926).

The increased solubility of the free silica in the fluoboric acid at higher temperature is undoubtedly due to hydrofluoric acid. Line and Aradine suggest that if the fluoride ion is removed from solution, that is, if its ionization, so-called, is depressed, it will have less effect on the free silica. They achieve this result by the addition of ferric chloride and phosphoric acid. The ferric ion very likely forms the complex ion FeF_6^{---}, or a ferric fluoborate, and the phosphoric acid reacts to form monofluorophosphoric acid:

$$2H_3PO_4 + H_2F_2 \rightleftarrows 2H_2PO_3F + 2H_2O$$

Both of these reagents do have the effect of reducing the solubility of free silica in fluoboric acid at higher temperatures. The color of the ferric ion has the additional advantage of indicating its absence as the color of the solution fades.

Calculation of Free Silica. Both the Knopf method and the fluoboric acid method of Line and Aradine for the estimation of free silica in the presence of silicates employ a correction factor to account for the solubility of free silica in the solvents used. In the Knopf method this solubility averages 0.7 per cent of the amount of free silica per day. In the fluoboric acid method this correction factor is 0.34 per cent per day.

In order to compute the mg. of quartz or free silica originally present from the mg. of free silica found in the residue, Kaplan and Fales[24] make use of the compound-interest law, also called the law of organic growth, or the snowball law, which may be expressed for rates of decrease by the differential equation

$$\frac{dy}{dx} = -ky$$

This expression is the first derivative of the exponential equation

$$y = y_0e^{-kx}$$

This may be expressed in the logarithmic form

$$\log y = \log y_0 - kx \log e$$

Applied to the solution of computing the amount of free silica originally present from the amount of free silica in the residue, the symbols of this equation have the following meaning:

y = mg. of free silica in residue
y_0 = mg. of free silica originally present
k = rate of loss, equivalent to 0.7 per cent per day in the Knopf method and 0.34 per cent per day in the fluoboric acid method

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[24] E. Kaplan and W. T. Fales, *Ind. Eng. Chem., Anal. Ed., 10*, 388 (1938).

x = time of action in days
$\log e = 0.43429$

For example, if in a determination of quartz in the presence of refractory silicates by the Knopf method, 500 mg. of dust required 10 days of treatment with hydrofluosilicic acid, leaving a residue corresponding to 50 mg. of quartz, then the amount of quartz originally present in the original sample of dust may be calculated as follows:

$$\begin{aligned} \log y_0 &= \log y + kx \log e \\ &= \log 50 + (0.007 \times 10 \times 0.43429) \\ &= 1.72937 \\ y_0 &= 53.63 \text{ mg.} \end{aligned}$$

The portion analyzed contained 53.63 mg. of free silica or quartz present, originally. This corresponds to 10.7 per cent of quartz in the portion of dust taken for analysis.

Where the error in estimating free silica is very large, because of improper sampling or for other reasons, calculation by use of this formula is unwarranted.

c. Rational Analysis

Shaw's Modification of Selvig's Method.[25,26] The principle for the rational analysis of materials for the determination of quartz is the attempt to remove from the sample all minerals except the quartz. The various minerals present are decomposed by suitable treatment with acids such as sulfuric and hydrochloric, and the products of decomposition are removed by solution in water and Lunge solution, which consists of 100 g. of crystallized sodium carbonate and 10 g. of sodium hydroxide dissolved in water and diluted to 1 liter. The decomposition of these minerals is seldom complete, with the result that the residue obtained after such treatment contains not only the quartz but also varying quantities of undecomposed silicates. A correction is usually made for the presence of these undecomposed minerals by assuming them to be orthoclase, the amount being calculated from the alumina present in the residue. In the case of shales and coal-measure rocks,[27] the error introduced is negligible.

Procedure. Grind 5 g. of the sample to pass a 60-mesh sieve. Mix with 300 ml. of dilute hydrochloric acid, 2.5 per cent by volume, and heat to boiling in a deep porcelain dish of 1,300 ml. capacity. Allow the dish to stand for 2 hours or until the material has settled, and siphon off the clear liquid. It is advisable to have a tap or pinch clamp in the siphon tube to reduce the rate of flow toward the end of the operation; if the siphon is clamped so that the end of the short limb is adjustable in the liquid, it will be found possible to remove practically the whole

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[25] A. Shaw, *Analyst, 59,* 446 (1934).
[26] W. A. Selvig, *Carnegie Inst. Tech., Mining Met. Invest., Bull. 21* (1925).
[27] F. H. Goldman, *U. S. Pub. Health Repts., 52,* 1702 (1937).

of the solution without disturbing the solid material. Stir the residue with 100 ml. of water, add 100 ml. of sulfuric acid (1:1), and boil the mixture. Stir frequently and boil until acid fumes are freely evolved. The temperature of the solution should not rise above 200° C. It is best to use a thermometer in order to keep a check on the temperature. The total time of the evaporation should be approximately 45 to 60 minutes. Allow the dish to cool for 30 minutes and dilute its contents with 1 liter of water. Stir well and allow to settle. Siphon off the clear solution. Treat the residue with 100 ml. of water and 100 ml. of sulfuric acid (1:1) and evaporate once more. After dilution, settling, and siphoning off the solution again, neutralize with Lunge solution. If the amount of acid liquid remaining in the dish is large, that is, of the order of 20 ml. or more, use 50 per cent sodium hydroxide solution for the neutralization in order to prevent excessive dilution of the Lunge solution in the following operation.

Add 300 ml. of Lunge solution and heat the liquid to boiling with frequent stirring. Allow the mixture to stand for 2 hours, siphon off the supernatant liquid, and boil the residue for 5 minutes with 500 ml. of concentrated hydrochloric acid. Dilute to 1 liter and allow to settle. Siphon off the acid solution, neutralize the remaining acid with Lunge solution or with 50 per cent sodium hydroxide solution, add 150 ml. of Lunge solution, and heat the mixture to boiling. Allow to stand for 2 hours. Siphon off the Lunge solution and boil the residue for 5 minutes with 200 ml. of concentrated hydrochloric acid. Add 200 ml. of water and filter the mixture through Whatman No. 40 filter paper. Transfer the residue to the filter, wash twice with hydrochloric acid (1:3), then with water until the washings are free from chlorides, and, finally, ignite to constant weight in a tared platinum crucible. To the ignited residue add 5 ml. of water, 5 to 10 drops of concentrated sulfuric acid, and 15 ml. of hydrofluoric acid. Evaporate the resultant mixture on a hot plate until sulfuric acid fumes are evolved. Repeat the evaporation with 2 further quantities of hydrofluoric acid, continuing the heating during the final evaporation until sulfuric acid fumes are *freely* evolved, to insure complete removal of fluorine, which would interfere with the determination of alumina in the residue.

Extract the contents of the crucible with water and filter the solution. Determine alumina in the usual way by precipitating with ammonia, using methyl red as an indicator to avoid excess.[28] The weight of alumina, multiplied by 5.41, gives the equivalent weight of potash feldspar, and this, subtracted from the weight of the ignited residue previously determined, gives the amount of quartz or free silica in the sample.

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[28] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929.

This method of rational analysis when applied to coal-measure rocks and shales tends to give low results, but the method can, in general, be relied upon to give results accurate within 2 per cent for these rocks.

d. Flotation Methods for Quartz[29]

Quartz may be separated from other minerals which differ from it in specific gravity by flotation, using various liquids of known specific gravity. Bromoform is one of the liquids commonly used. Others[30] have used a mixture of acetylene tetrabromide, that is, tetrabromoethane, and ethylene bromide. The dust is treated with sulfuric acid, dried, and then centrifuged in this mixture, whose specific gravity approaches that of quartz, 2.65. By centrifuging at great speed, 10,000 r. p. m., it is possible to remove everything under 2.63. The remaining particles are examined for quartz.

e. Micro Method for Silica in Dust[31,32]

Place 5 to 10 mg. of dust in a tared platinum crucible of 2 to 3 ml. capacity. Determine the loss on heating at 100° C. and the loss on ignition. Fuse the dust with 3 to 4 times its weight of sodium carbonate. Take up the melt in 1 ml. of water and neutralize without danger of squirting by exposing it to the acid vapor from a small dish of hydrochloric acid warmed slightly on the top of an air oven run at 100° C. Support the crucible in a small triangle resting on the dish of acid and cover both with a large crystallizing dish or a small bell-jar. Render the silica insoluble by evaporation 3 times with hydrochloric acid, followed each time by drying for 20 minutes at 105° C. Take up the residue in water containing about 0.25 ml. of hydrochloric acid and filter through a King[33] filter stick into a glass micro beaker for other determinations such as iron or aluminum if desired.

Ignite the insoluble matter, cool, and weigh. Volatilize the silica by treatment with hydrofluoric acid and evaporate in the presence of water containing dilute sulfuric acid. Finally, ignite the crucible for 2 minutes and reweigh. Nitric acid may also be used for the dehydration of the silica.

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[29] F. H. Goldman, *U. S. Pub. Health Repts.*, *52*, 1709 (1937).
[30] F. Sartorius and K. W. Joetten, *Arch. Hyg. Bakt.*, *115*, 135 (1935).
[31] J. W. Matthews, *Analyst*, *63*, 467 (1938).
[32] H. Thurnwald and A. A. Benedetti-Pichler, *Mikrochem.*, *11*, 200 (1932).
[33] E. J. King, *Analyst*, *58*, 325 (1933).

King Filter Stick. The filter stick of Emich[34,35] and other microanalysis has been modified by King[36] to make it suitable for silica determinations.

A thick-walled capillary tube, of about 0.5 cm. diameter and with a bore of about 1 mm., is pulled out slightly at one end and cut off smoothly at the other end at a length of about 10 cm. A piece of ordinary glass tubing of 5 or 6 cm. length is selected to fit snugly around the first tube. The glass tubes are held telescoped together by a piece of rubber tubing fitted around the inner tube 3 or 4 cm. below the pull-out end and over the end of the outer tube. The inner tube can now be pushed back and forth within the outer tube while they remain held together by the rubber collar. The inner tube is so adjusted that its broad end is about 2 mm. within the opening of the outer tube. In the shallow cavity thus formed is inserted a roll of ashless filter paper, made by rolling up two or three strips of paper about 7 cm. long, or a disk of filter paper fiber, which can be made very conveniently by cutting out a circle from a Fisher's ashless filter-paper "accelerator" with a cork borer of the correct diameter. Fisher's "accelerators" are small squares of pressed filter-paper fiber of approximately 1 mm. thickness. When shaken with water these disintegrate and form a uniform suspension of paper fiber. Any crevices in the filter-paper roll or at the edge of the disk can be filled by sucking in a little filter-paper fiber suspended in water.

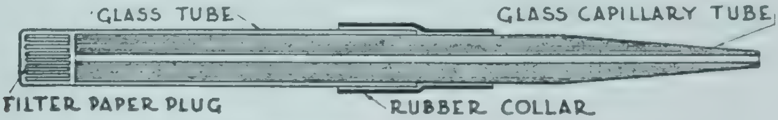

Fig. 75. King filter stick.

After filtering the supernatant solution and washings in the silica determinations through the filter stick, the plug of filter paper is pushed out into the crucible by moving down the inner tube through the rubber collar of the filter stick. Any particles of silica adhering to the glass are washed down into the crucible with the aid of a wash bottle.

f. Interpretation of Silica Results

Care should be taken in calculating the quartz content of a material from its chemical analysis. Calculations based on formulas for certain minerals as given in texts on mineralogy should seldom be made,[37] for such formulas are empirical and may refer only to a particular sample from some definite locality, or they may refer to an ideal formula for the pure mineral. It is best to analyze the particular mineral from which the

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[34] F. Emich, *Lehrbuch der Mikrochemie,* Bergmann, München, 1926

[35] A. A. Benedetti-Pichler, *Z. anal. Chem., 64,* 409 (1924).

[36] E. J. King, *Analyst, 58,* 325 (1933).

[37] F. H. Goldman, *U. S. Pub. Health Repts., 52,* 1702 (1937).

dust arises and then apply the results of the analysis for the required calculations. Even this should be done with caution.

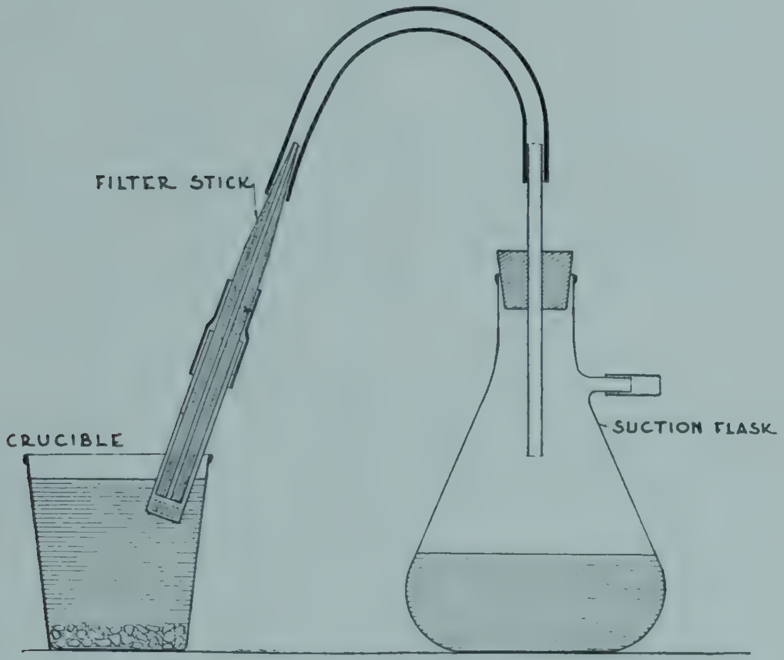

Fig. 76. Filtration operation with King filter stick.

The hydrofluosilicic acid method is inaccurate[38] for such materials as shale, clay, pumice, etc., when compared with the petrographic method. The method should be used only on 150-mesh material. Garnet, sillimanite, zircon, beryl, forstirite, and dumortierite are not completely decomposed by the fluoboric acid method.[39] Shaw's method is applicable only for coal-measure rocks and shales.[40]

It is clear from a consideration of these methods that they are not completely adequate for dust determinations, since the median size of industrial dust samples runs below 10 μ. For rafter samples, it is about 7 μ, while quartz ground to pass a 200-mesh sieve has a median size of 65 μ. It is therefore necessary to run controls on quartz having the same particle-size distribution as the sample to be analyzed, in order to determine whether the correction for the solubility of the quartz will be small enough to insure reasonable accuracy.

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[38] H. L. Ross and F. W. Sehl, *Ind. Eng. Chem., Anal. Ed.*, *7*, 30 (1935).
[39] W. R. Line and P. W. Aradine, *Ind. Eng. Chem., Anal. Ed.*, *9*, 60 (1937).
[40] A. Shaw, *Analyst*, *59*, 446 (1934).

Petrographic analysis should always be made and a complete chemical analysis is also valuable, as the total silica content alone gives the upper limit for the amount of free silica present. With judgment, a certain minimum amount of silica necessary for combination with the other elements may be calculated.

By judicious sampling it is possible to overcome many of the difficulties inherent in the analysis of dusts for free silica. The more information the analyst can obtain concerning the sample, the easier it is for him to make a satisfactory analysis. Goldman[41] recommends the accompanying form, which is designed to provide such information.

DUST SAMPLE SUBMITTED FOR ANALYSIS

Sample number _ _ _ _ _ _ **Industry** _ _ _ _ _ _ _ _ _ _ **Location** _ _ _ _ _ _ _ _ _

Where was sample collected? _ _ _ _ _ _ _ _ _ _ (Name of factory, quarry, mine, etc.)

What process was carried on where this sample was collected? _ _ _ _ _ _ _ _ _ _ _ _

Method used for collecting sample _

From what material did this dust presumably arise? _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _
(Samples of coarse material should be submitted, together with any available analytical data)

IF SAMPLE IS OF MINERAL ORIGIN
Name of principal mineral _
Location of deposit _
Name of deposit (vein, dike, bed, etc.) _
Size of deposit _
Associated gangue materials _
Geological description of area _

ADDITIONAL INFORMATION

Date _ _ _ _ _ _ _ _ _ _ _ _ Collected by _ _ _ _ _ _ _ _ Submitted by _ _ _ _ _ _

Supplementing the actual dust sample, samples of all the materials from which the dust may presumably have arisen should be obtained. Such materials will usually prove amenable to analysis, whereas the dust itself may not. In many cases it happens that the dust sample has practically the same chemical composition as the parent material. In any case excess sampling is not of great moment, but the lack of a particular sample may make itself keenly felt.

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[41] F. H. Goldman, *U. S. Pub. Health Repts.,* *52,* 1702 (1937).

g. Estimation of Dissolved Silica

Solutions containing dissolved silica react with acid solutions of ammonium molybdate to form colored silicomolybdates.[42] A bibliography of the literature on the colorimetric determination of silica is given by Schwartz.[43]

Reagents. Sodium Hydroxide-Borate Buffer Solution.—Solution A: Dissolve 12.4 g. of boric acid in water, add 100 ml. of N sodium hydroxide solution, and dilute to 1 liter.

Solution B: Prepare a 0.1 N solution of sodium hydroxide. Add 6 parts of solution A to 4 parts of solution B to prepare the buffer solution. Keep in a hard rubber bottle.

Standard Picric Acid Solution. Dissolve 102.4 mg. of pure picric acid in water and make up to 100 ml. Diluting 1 part of this stock solution to 100 parts with water yields a solution 50 ml. of which has the same quality and intensity of color as that developed in a solution containing 1 mg. of silica when treated with 2 ml. of 10 per cent ammonium molybdate solution and 4 drops of sulfuric acid and then made up to 50 ml. Two ml. of ammonium molybdate solution is sufficient for 3.5 mg. of silica but not more.

Potassium Chromate Standard. Dissolve 0.63 g. of potassium chromate in water and dilute to 1 liter. One ml. of this solution diluted with 50 ml. of a 1 per cent solution of sodium tetraborate, $Na_2B_4O_7.10H_2O$, or other appropriate buffer and enough water to make a total of 100 ml. is equivalent to 1 part per million of silica. Aliquots of this solution ranging from 0.0 to 15.0 ml. when diluted with 25 ml. of a 1 per cent borax solution and sufficient water to make 55 ml. are equivalent to 2 parts per million of silica per ml.[44]

Procedure.[43] To 110 ml. of the test solution add 50 ml. of sodium hydroxide-borate buffer solution, 2 ml. of 1 M calcium chloride solution, and stir vigorously. A flocculent precipitate of calcium phosphate forms, which settles rapidly. Allow the solution to stand for 2 hours with occasional stirring, and then filter. To 50 ml. of the filtrate add 2 ml. of 10 per cent ammonium molybdate solution, 100 g. of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, dissolved in water and made to 1 liter. Add 1 ml. of hydrochloric acid (3:2). Allow the solution to stand for 10 to 15 minutes and compare with an appropriate potassium chromate or picric acid standard. Subtract the buffer blank from the observed reading and multiply the result by the dilution factor 1.54.

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[42] E. J. King, *J. Biol. Chem., 80,* 25 (1928).

[43] M. C. Schwartz, *Ind. Eng. Chem., Anal. Ed., 6,* 364 (1934); *14,* 893 (1942).

[44] H. W. Swank and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed., 6,* 348 (1934).

7. Physical Chemical Methods

Both the petrographic and the chemical methods for the estimation of free silica in dusts and rock have their limitations, as has been discussed. Bale and Fray,[45] Clark and Reynolds,[46] and Ballard and Schrenk[47] have described x-ray diffraction methods for the quantitative analysis of dusts.

Hull[48] pointed out a number of facts concerning the diffraction of x-rays by powdered crystalline materials. Of these the most important is that each crystalline chemical compound, when pulverized and placed in a monochromatic beam of x-rays, gives rise to a "diffraction pattern," which may be registered photographically and which is unique for that compound. The same compound always gives rise to the same diffraction pattern, which is different from the pattern obtainable from any other compound or from an allotropic modification of the same compound. For a mixture of crystalline materials, each substance present gives its own pattern, regardless of the presence of the other components, and the resultant pattern is the sum of the patterns of all the component compounds. By proper resolution of such a complex pattern into its constituent parts, it is found that x-ray diffraction is a most powerful method of qualitative analysis, in that it shows not only the elements present but also their true state of chemical combination.

If the sample is not received as a powder, it is thoroughly ground, a small portion is shaped into a wedge, and it is set in the camera, which has a strip of film placed flush against its cylindrical wall. A narrow beam of x-rays emerging from a small window is directed against the sample. The rays diffracted by the sample impinge on the film to yield a picture of lines varying in intensity, which is characteristic for different substances, as mentioned previously. The density of these lines may be measured by the use of a microphotometer and recorded.

Clark and Reynolds[49] developed a method which is a modification of the "internal-standard" method of ultraviolet spectroscopy applied to the Hull method of x-ray diffraction by a crystalline powder. A pure crystalline powder, known not to be present in the mixture being examined, is

[45] W. F. Bale and W. W. Fray, *J. Ind. Hyg.*, *17*, 30 (1935).

[46] G. L. Clark and D. H. Reynolds, *Ind. Eng. Chem., Anal. Ed.*, *8*, 36 (1936).

[47] J. W. Ballard and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest.* 3888 (1946).

[48] A. W. Hull, *J. Am. Chem. Soc.*, *41*, 1168 (1919).

[49] G. L. Clark and D. H. Reynolds, *Univ. Toronto Studies, Geol. Ser.*, *38*, 13 (1935).

added to the unknown in a definite ratio and the x-ray diffraction pattern registered by a suitable apparatus. The ratio of the density of a line of the substance sought to that of a nearby line of the added standard is determined photometrically. The ratio thus obtained is proportional to the line intensity of the substance sought, which in turn is proportional to the amount of substance in the mixture. By reference to a curve prepared empirically using mixtures of known composition, the percentage of the component sought is obtainable.

For the registration of the diffraction pattern, a circular reflection type camera, shown diagrammatically in Figure 77, may be used. The samples of natural ores and mine dusts or other dusts should first be ground to pass a 200-mesh sieve and then should be ground further by a steel-ball mill, using ball bearings in a cylindrical steel case, of such size that samples 1 gram in size can be handled without appreciable loss. Twenty-four hours of grinding is necessary to reduce quartz that has already passed a 200-mesh screen to a powder of the required fineness.

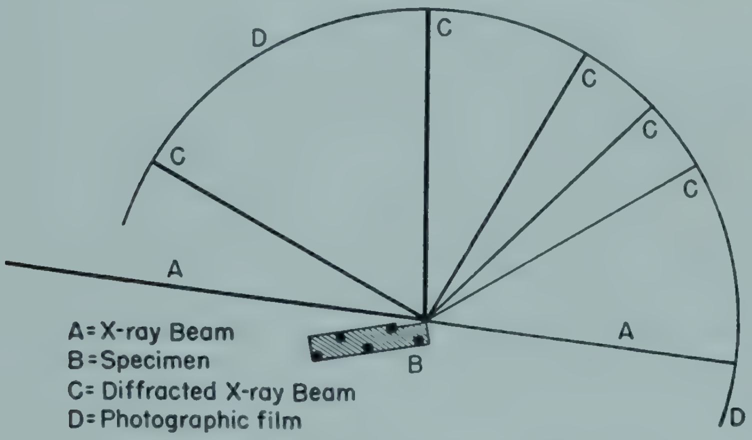

Fig. 77. Diagram of x-ray diffraction camera.[46]

The extra grinding insures a homogeneous sample. It is very important to make the specimen homogeneous because the amount of sample actually bathed by the x-ray is somewhat less than 1 mg.

Procedure. Press the specimen being examined into the shape of a wedge and mount it so that the tip of the wedge falls at the center of the camera. Bathe the tip of the wedge by the lower half of the main x-ray beam, which is defined with the aid of a series of lead pinholes 0.075 cm. (0.030 inch) in diameter. Register the resulting diffraction pattern on a photographic film held tightly against the outside of a machined circle of which the tip of the wedge is the geometric center. It may be observed that in certain directions from the wedge there is a focusing effect which causes a narrowing of the diffraction lines in those directions. By taking advantage of this, a high degree of resolution can be obtained in any desired portion of the pattern, together with a rather uniform background blackening in the region particularly to be investigated.

The type of camera to be used in this work should have an arrangement so that the wedge-shaped sample may be revolved about its tip. This permits the side of the wedge next to the x-ray tube to be inclined at any angle to the incident beam of x-rays, so that the maximum effect of the focusing may be realized. Results may be duplicated exactly because the shape of the specimen is always the same, it can be set at the same angle to the beam every time, and all parts of the camera are permanently fixed with respect to each other and may be locked into position on the instrument table, so that conditions surrounding the registration of the diffraction pattern may be maintained at maximum constancy.

The sample may be irradiated with a Philips Metalix fine-structure research x-ray tube with copper anode, mounted in a Hayes x-ray spectrograph, operating at 30 kvp. and 25 milliamperes. The exposure time is varied from 1 to 6 hours, depending upon the concentration range of the specimen being examined, those samples having the lowest percentages of the substance sought requiring the longer exposures. The amount of the substance being estimated is then obtained by having the principal lines of the diffraction pattern photometered and compared with the standard or reference. The ratios thus obtained are proportional to the relative intensities of the line, and hence to the concentration of the substance sought in the specimen.

Bale and Fray[50] use a somewhat different technique. The dust is finely ground and is placed in a capillary glass tube. The properly filtered K radiation of a molybdenum-target x-ray tube is used to produce a nearly monochromatic beam, which is passed through the contents of the capillary tube. This procedure produces diffractive effects that are identified on a film as bands of different intensity and density, separated by areas of comparatively clear film. Comparison is made with known spectra. The quantitative estimation may be made by comparing the relative film densities of selected strong bands of the substance in a mixed sample with that of a known mixed control of the same substances.

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[50] W. F. Bale and W. W. Fray, *J. Ind. Hyg.*, *17*, 30 (1935).

Ballard and Schrenk[51,52] revised the internal-standard method by use of two internal standards yielding five lines (two for calcium fluoride and three for nickel oxide) for comparison with four lines of quartz. By use of the five lines of the two internal standards, it was usually possible to have one or more free from interference with other diffraction lines. A microphotometer record of the diffraction pattern was used to obtain the heights, that is, the relative intensities, of the quartz lines compared to the standard lines.

For further information concerning chemical analysis by x-ray diffraction, the reader is referred to the work of Hanawalt, Rinn, and Frevel,[53] the American Society for Testing Materials,[54] to Clark,[55] to Davey,[56,57] and to Frevel.[58]

The quartz or free-silica content of dusts may be estimated by petrographic, fusion, chemical, physical chemical, or a combination of petrographic and chemical methods. Each method has its advantages and disadvantages. The petrographic method can best be applied to thin sections of the raw material. X-ray diffraction methods must be applied to very finely ground powders. X-ray methods require rather expensive apparatus. The combination of the petrographic and chemical methods provides good information and serves as a check upon the progress of the chemical method.

It is well to recall that danger from free silica, with subsequent production of fibrosis and silicosis, is by no means limited to rock drilling, quarrying, or even foundries. Silica occurs not only in minerals but is also present in vegetable and animal matter. The straw from bamboo and from the grains that are used to make cereals contains fairly large quantities of silica. The common horsetail weed has a large siliceous skeleton. The feathers of birds contain silica and it also occurs in animal remains such as kieselguhr, which consists of the siliceous skeletons of extinct diatoms and is almost pure silica. All of these products are used in industry and hence all of them may provide a silica hazard.

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[51] J. W. Ballard, H. I. Oshray, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3520* (1940).

[52] J. W. Ballard and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3888* (1946).

[53] J. D. Hanawalt, H. W. Rinn, and L. K. Frevel, *Ind. Eng. Chem., Anal. Ed., 10,* 457 (1938).

[54] Am. Soc. Testing Materials, *Symposium on Radiography and X-Ray Diffraction Methods* (1937).

[55] G. R. Clark, *Applied X-Rays,* McGraw-Hill, New York, 1932.

[56] W. P. Davey, *Study of Crystal Structure and Its Applications,* McGraw-Hill, New York, 1934.

[57] W. P. Davey, *J. Applied Phys., 10,* 820 (1939).

[58] L. K. Frevel, *Ind. Eng. Chem., Anal. Ed., 16,* 209 (1944).

8. Asbestos

Asbestos is the class name for several different fibrous minerals, but commercial asbestos[59, 61] is mainly the fibrous form of serpentine known as chrysotile. One of the most important industrial uses of this substance is in the manufacture of fire-resistant textiles. Chrysotile is a hydrous magnesium silicate, $3MgO.2SiO_2.2H_2O$, or $Mg_3Si_2H_4O_9$, containing 44.1 per cent of silica, 43.0 per cent of magnesia, and 12.9 per cent of water. Other types of asbestos often contain silicates of iron, calcium, and aluminum, as well as magnesium.[62]

Asbestos dust can be trapped with an impinger dust-sampling apparatus using 25 per cent aqueous ethyl alcohol as the collecting medium. This solution prevents flocculation of the dust particles without causing excess evaporation in either the sampling flasks or counting cells. Samples may be counted by the light-field technique detailed on page 144, using the modified ocular micrometer disk (Fig. 67). The dust in 20 to 30 cubic feet of air should be sampled.

The safe threshold value for asbestos dust exposure is considered 5 million particles per cubic foot.[61] Values are given in Table 7, Appendix.

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"Report of Sub-Committee on Dust Procedures in Air Analysis. Review and Discussion of Methods of Analyzing Industrial Dusts," *Am. Pub. Health Assoc. Yearbook 1937–38,* 85.

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[59] R. T. Page and J. J. Bloomfield, *U. S. Pub. Health Repts., 52,* 1713 (1937).

[60] H. Ries and T. L. Watson, *Engineering Geology*, Wiley, New York, 1737.

[61] R. R. Sayers and W. C. Dreessen, *Am. J. Pub. Health, 29,* 205 (1939).

[62] W. B. Fulton, A. Dooley, J. L. Matthews, and R. L. Houtz, *Pennsylvania Dept. Labor Ind., Special Bull. 42* (1935).

Ries, H., and T. L. Watson, *Engineering Geology,* Wiley, New York, 1937.

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CHAPTER VII

Lead, Mercury, and Arsenic

From the broad point of view, almost every metal or metallic compound encountered in manufacture and industry presents some type of industrial hazard. From the more realistic point of view, the important metallic industrial hazards are lead, mercury, arsenic, chromium, cadmium, antimony, and their compounds. Of lesser importance, although not necessarily any the less hazardous, may be mentioned manganese, vanadium, tellurium, thallium, selenium, nickel, zinc, copper, tin, and their compounds. As a general rule it may be stated that all of these metals are much more hazardous in their compounds than the metal itself, except in the case of fumes, and that the more soluble the compound, the more poisonous it is likely to be. As an example, men are often badly poisoned when mining carbonate or oxide ores of lead, whereas lead poisoning is rare among men mining only lead sulfide (galena).[1]

The damage produced by inhalation is much more severe than that produced by swallowing. Lead poisoning is rated as 10 times more liable to occur from breathing lead dust than from swallowing it. This is probably so because the liver filters out swallowed substances like lead and removes them from the blood before harm can be done. If they are breathed, they are taken up by the blood stream, pumped all over the body, and thus make themselves felt more readily than would otherwise be possible.[2]

A. LEAD

Plumbism was known in Biblical times. Hippocrates (about 460–357 B.C.) described the illness as a result of working in the smelting of lead ores and other metal ores. The alchemists and early metallurgists were well aware of it. Ramazzini describes the symptoms of lead encephalopathy in his book, *Diseases of Tradesmen,* in 1700. The history of lead poisoning is discussed by Teleky.[3] A general discussion is given by Cantarow and Trumper.[4]

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[1] R. R. Sayers, *U. S. Bur. Mines, Rept. Invest. 2660* (1924).

[2] P. Drinker, *Ind. Med., 4.,* 253 (1935).

[3] L. Teleky, *Ind. Med., Ind. Hyg. Section, 9,* 17 (1940).

[4] A. Cantarow and M. Trumper, *Lead Poisoning,* Williams & Wilkins, Baltimore, 1944.

While deaths from this disease have practically disappeared from industry[5] and cases of acute lead poisoning are far less frequent than they were a decade ago, there are still large numbers of cases of lead poisoning of the subacute and chronic types. The prevention of lead poisoning is largely a matter of adequate sanitary engineering and medical discipline. It rests essentially upon the elimination of lead-bearing fumes, discipline as to cleanliness, and medical supervision of exposed workers.[6,7]

1. Lead Compounds in Industry

Among the more important lead compounds to which workers are exposed are lead fume and dust in the melting of lead; lead carbonate, lead sulfate, red lead, and lead chromate in the pigment industry; lead arsenate dust in the manufacture and use of insecticides; lead silicate in the pottery industry; litharge, red lead, and lead peroxide in the storage-battery industry; and the sulfide, carbonate, and oxide of lead in the mining and milling of lead ore.[8] Other lead compounds met in industry are lead suboxide, lead sesquioxide, basic lead carbonate, lead acetate, lead chloride, lead nitrate, and tetraethyl lead.

These compounds generally enter the body by way of the respiratory tract and the gastrointestinal tract. The portal of entry of lead into the system in industrial exposure chiefly associated with lead poisoning is now generally conceded to be the respiratory tract rather than the alimentary tract.[9]. However, it is to be noted that tetraethyl lead is a lipoid solvent and therefore can be absorbed through the skin. Furthermore, when tetraethyl lead is exposed to sunlight or is allowed to evaporate, it decomposes and forms as one of its decomposition products triethyl lead, which is a poisonous compound.

2. Toxicity of Lead Compounds

The importance of the lead hazard from an economic point of view may be shown by the time spent on compensation in a certain plant. In the mixing department of a storage-battery plant the compensation cases rose to the level of 33 per cent in the third month of exposure to lead.[10]

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[5] M. R. Mayers and M. M. McMahon, *N. Y. State Dept. Labor, Special Bull. 195* (1938).

[6] J. C. Aub, L. T. Fairhall, A. Minot, and P. Reznikoff, *Medicine, 4*, 1 (1925).

[7] P. Drinker, *J. Ind. Hyg., 7*, 531 (1925).

[8] L. T. Fairhall, R. R. Sayers, and J. W. Miller, *U. S. Pub. Health Service, Bull. 253* (1940).

[9] F. B. Flinn, *J. Ind. Hyg., 8*, 51 (1926).

The toxicity of lead compounds is influenced by a number of factors, among which may be mentioned solubility in body fluids, length of time in contact with body fluids, quantity ingested, inhaled, or absorbed, and the quantity present in the circulation at a given time. Lead is thought to be toxic only when present in the systemic circulation. Thus it can be stored by the body and only becomes a danger when it is returned to circulation in greater amounts than the body can safely eliminate.[11]

a. Solubility of Lead Compounds

One of the significant factors of lead poisoning is the failure to realize that a lead compound that is insoluble in water may not necessarily be insoluble in the fluids of the body. This can be seen readily from Table 7.

TABLE 7
Solubility of Lead Compounds

Compound	In serum at 25° C., mg./liter	In water, mg./liter
Lead monoxide, PbO (litharge)	1,152.0	17.1
Lead	578.0	—
Lead sulfate, $PbSO_4$	43.7	44.0
Lead carbonate, $PbCO_3$	33.3	1.7
Lead chromate, $PbCrO_4$	...	0.01

Lead peroxide is slightly soluble in sulfuric acid and is insoluble in water.[12,13] Its solubility in blood serum has not been studied.

b. Relative Toxicity of Lead Compounds

Fairhall and Sayers,[14] using the storage of lead in bone tissue as an index of the extent to which the system of guinea pigs was flooded with lead in a given space of time, and considering the relationship of other factors indicating possible damage, arrange the toxicities of various lead compounds into two groups, those more toxic and those less toxic. The arrangement is shown in Table 8.

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[10] *U. S. Pub. Health Repts., 48,* 1043 (1933).

[11] M. R. Mayers and M. M. McMahon, *N. Y. State Dept. Labor, Special Bull. 195* (1938).

[12] J. C. Aub, L. T. Fairhall, A. Minot, and P. Reznikoff, *Medicine, 4,* 1 (1925).

[13] A. E. Russell, R. R. Jones, J. J. Bloomfield, R. H. Britten, and L. R. Thompson, *U. S. Pub. Health Service, Bull. 205* (1933).

[14] L. T. Fairhall and R. R. Sayers, *U. S. Pub. Health Service, Bull. 253* (1940).

c. Lead Standards

Legge[15] stated that 2 mg. of lead per day is the lowest dose that when inhaled as dust fumes may in the course of years set up lead poisoning. Oliver[16] concluded that 1 mg. of ingested or inhaled lead causes plumbism. Greenburg[16] and his co-workers found that employees exposed to an average amount of 0.009 mg. of lead per cubic foot of air do not present evidences of chronic lead poisoning when the duration of exposure is $1^1/_2$ years or less but when the duration at such an occupation is $2^1/_2$ years or more, evidences of chronic lead poisoning are present. They conclude that, based on Legge's figures for the amount of air respired in a working day of 8 hours, air analyses in the casting shop of a lead-battery plant indicate that inhalation of 1.45 mg. of lead per day produces lead poisoning within $2^1/_2$ years.

TABLE 8

Relative Toxicity of Lead and Its Compounds

	Method of introduction		
Order of toxicity	Injection	Ingestion	Inhalation
Most toxic	Lead arsenate	Lead arsenate Lead carbonate Lead monoxide Lead sulfate	Lead carbonate Lead monoxide
Of similar but lower degree of toxicity	Metallic lead Lead carbonate Lead chromate Lead monoxide Red lead Lead dioxide Lead phosphate Lead sulfate Lead sulfide	Metallic lead Lead chromate Red lead Lead dioxide Lead phosphate Lead sulfide	Metallic lead[a] Lead arsenate[a] Lead chromate Red lead Lead dioxide Lead phosphate Lead silicate Lead sulfide

[a] Inconclusive.

The generally accepted standard for the lead concentration in a permissible working atmosphere is 0.15 mg. per cubic meter, as shown in

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[15] T. M. Legge and K. W. Goadby, *Bleivergiftung und Bleiaufnahme*, Berlin, 1921.

[16] L. Greenburg, A. A. Schaye, and H. Shlionsky, *U. S. Pub. Health Service, Reprint 1299* (1929).

Table 6, Appendix. A study of the toxicity of lead chromate led Harrold[17] and his co-workers to conclude that in the case of insoluble compounds like lead chromate the level of lead allowable in the atmosphere should be raised. From his investigation Kehoe[18] concluded that the daily ingestion of slightly more than 2 mg. of lead, for a period of more than 1 year, failed to result in any demonstrable effect upon the health or well-being of a healthy adult, but it induced a level of lead elimination higher than that caused by the ingestion of 1 mg. daily and a slightly greater rate of lead retention in the tissues.

The U. S. Food and Drug Administration of the Federal Security Agency, taking into consideration the changed views on the toxicity of ingested lead, has raised the tolerance on lead spray residue from the 3.58 parts per million (0.025 grain per pound) to 7.15 parts per million (0.05 grain per pound).[19]

The minimal amounts of lead normally present in the atmosphere of industrial establishments are 0.10 mg. per 10 cubic meters, generally, and 0.13 mg. per 10 cubic meters in auto-repair shops. At congested street intersections the corresponding concentration is 0.09 mg. per 10 cubic meters.[20]

3. *Determination of Lead*

The literature contains numerous methods for the detection and estimation of lead. With the realization of the danger from continual inhalation, ingestion, and absorption of even small amounts of lead has come the development of methods by which one can estimate extremely small quantities of lead, that is, of the order of 1 γ, with great accuracy. Not all of the methods can conveniently be detailed here and consequently only the various types of chemical methods will be described. A comprehensive review of the preferred methods for the determination of lead in air and in biological materials has been prepared by the Subcommittee on Chemical Procedures of the Committee on Ventilation and Atmospheric Pollution of the Industrial Hygiene Section of the American Public Health

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[17] G. C. Harrold, S. F. Meek, G. R. Collins, and T. F. Markell, *J. Ind. Hyg. Toxicol.*, *26*, 47 (1944).

[18] R. A. Kehoe, J. Cholak, D. M. Hubbard, K. Bambach, R. R. McNary, and R. V. Story, *Experimental Studies on the Ingestion of Lead Compounds*, Kettering Laboratory of Applied Physiology, University of Cincinnati, 1940.

[19] Federal Security Agency, Social Security Board, Washington, D. C., August 10, 1940.

[20] J. J. Bloomfield and H. S. Isbell, *J. Ind. Hyg.*, *15*, 144 (1933).

Association.[21] Another review is given by Jacobs.[22] The preferred physical method is the spectrographic method.

The choice of a procedure for the estimation of lead is dependent on a number of factors, the principal ones being the equipment available, the order of the quantity of lead being estimated, and the preference of the analyst. The methods generally used can be classified as follows:

Large and Medium Quantities of Lead:

(1) Precipitation and estimation as lead sulfide.

Medium and Small Quantities of Lead:

(2) Precipitation of lead as sulfide, then as chromate, and estimation with *s*-diphenylcarbazide or by iodide-thiosulfate titration.

Minute Quantities of Lead:

(3) Extraction with dithizone and colorimetric, photometric or indirect estimation by titration of the dithizone that combines with lead.

These methods are the most widely used and the last method is particularly suitable when photometric and colorimetric equipment are not available.

(4) Coprecipitation of lead and copper, separation of lead by electrolysis as peroxide and estimation by iodometric titration.

(5) A combination of the dithizone and electrolytic methods.

Polarographic methods for the estimation of lead are described by Kolthoff and Lingane,[23] by Feicht, Schrenk, and Brown,[24] and by Goldman and May.[25]

It is clear that in making analyses for micro quantities of lead it is essential that all the equipment, glassware, and reagents be as free of lead as possible. This reduces possible sources of contamination and minimizes the blank. The water used in the analyses must be distilled water, preferably redistilled or treated so as to be lead-free. The glassware should be Pyrex or a similar type glass. New silica dishes should be ignited and treated with hot hydrochloric acid before use. Reagents such as hydrochloric acid, nitric acid, ammonium hydroxide, and chloroform should be redistilled and stored in Pyrex glassware. Filter papers should be soaked overnight in nitric acid (1:1,000) and then washed free of lead and acid, using large volumes of water with the aid of a Büchner funnel and suction. The papers may be dried in a vacuum desiccator over sulfuric acid to avoid the brittleness induced by drying in an oven. It is good practice in the dithizone method to give the glassware used an additional washing with a mixture of 50 ml. of nitric acid (1:1,000), 10 ml. of ammonia-cyanide mixture, and a few ml. of dithizone in chloroform solution. Then rinse thoroughly with lead-free water. In other methods, in addition to the usual treatment with cleaning solution, washing, etc., the glassware should be rinsed thoroughly with tap water, distilled water, and lead-free water.

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[21] F. H. Goldman, A. A. Coleman, W. G. Fredrick, A. N. Setterlind, H. H. Schrenk, and J. Cholak, *Methods for Determining Lead in Air and in Biological Materials*, Am. Pub. Health Assoc., New York, 1944.

[22] Morris B. Jacobs, in A. Cantarow and M. Trumper, *Lead Poisoning*, Williams & Wilkins, Baltimore, 1944.

[23] I. M. Kolthoff and J. J. Lingane, *Polarography*, Interscience, New York, 1941.

[24] F. L. Feicht, H. H. Schrenk, and C. E. Brown, *U. S. Bur. Mines, Rept. Invest.* 3639 (1942).

[25] F. H. Goldman and I. May, *Ind. Hyg. Quarterly*, 7, No. 3, 21 (1946).

a. Sampling

If a sample under examination is in solid form, it should be pulverized to pass through a 100-mesh sieve. A representative specimen, containing not more than 0.2 mg. lead, should then be taken for analysis, if one of the methods designed for smaller quantities of lead is used.

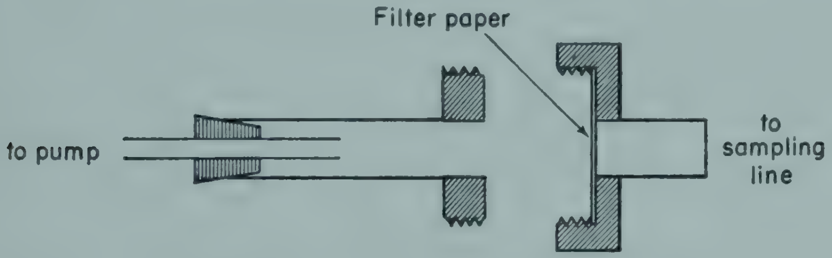

Fig. 78. Filter device for lead fumes and dust.

Lead fumes and lead dust in the atmosphere of the workshop may be sampled as described in Chapters II, IV, and V. The Greenburg-Smith impinger gives excellent results with lead dusts.[26,27] Nitric acid (1:99) may be used as the collection medium. Electric precipitators are preferable for the collection of fumes. Filtration devices are also used for fumes and dusts. Fairhall and Sayers[28] use the filtering device shown in Figure 78. The filter-paper devices of Brown, of Silverman and Ege, and of Bayrer and Hough have been previously described (see pages 125 and 126).

[26] L. Greenburg, A. A. Schaye, and H. Shlionsky, *U. S. Pub. Health Service, Reprint 1299* (1929).

[27] S. H. Katz, E. G. Meiter, and F. W. Gibson, *U. S. Pub. Health Service, Bull. 177* (1928).

[28] L. T. Fairhall and R. R. Sayers, *U. S. Pub. Health Service, Bull.* 253 (1940).

When the electric precipitator is used for the collection of fumes, a convenient procedure is sampling for $23^1/_2$ minutes at a rate of 3 cubic feet per minute. This is equivalent to a total sample of 2 cubic meters, which makes the calculations of results simpler.

The Greenburg-Smith impinger has a varying efficiency in the collection of lead fumes, which depends on the sampling flow rate. Thus, at sampling rates of 28.3 l. p. m. the efficiency of a single large impinger ranged from 21 to 53 per cent, and for two impingers in series from 55 to 60 per cent. The efficiency of a single midget impinger ranged from 13 to 21 per cent.[29] It was shown by Keenan and Fairhall[30] that the efficiency of the large impinger could be brought to nearly 100 per cent by increasing the sampling flow rate to 1.5 c.f.m., thus insuring impingement of the fume particles against the plate.

Sampling may also be performed by passing air at a rate of 200 to 300 ml. per minute through two absorbers in series containing 10 per cent nitric acid.

The general procedure, using the all-glass Greenburg-Smith impinger, is to trap the lead dust in 250 ml. of lead-free water. Some lead compounds require collection in a dilute nitric acid solution. In this case 10 ml. of nitric acid, sp. gr. 1.42, in 250 ml. of water is adequate. If modified impingers of this type are used that require less absorbing solution, the amount of acid added should be known, for it is important if the dithizone method is to be used. Since the sampling rate with the Greenburg-Smith impinger is generally kept slightly below 1 c. f. m., in order to obtain a sample of 1 cubic meter from 30 to 40 minutes should be allotted for the sampling. It may be necessary to sample as much as 60 to 90 cubic feet or as little as 10 cubic feet, depending, of course, entirely on the lead content of the air being sampled. The samples should be taken at positions which make them representative of the general conditions of the workroom or of the air breathed by the worker. If the dithizone method is to be used, the sample should not exceed 0.1 mg. of lead.

Preparation of Sample. If the electric precipitator has been used for sampling, close one end of the precipitator tube with a tight-fitting Davel rubber cap.[21] Add 50 ml. of nitric acid (1:19) and rub the sides with a rubber policeman. Transfer the acid to a Pyrex beaker, add an additional 50 ml. of nitric acid (1:19), and after scrubbing the tube transfer to the

[29] J. B. Littlefield, F. L. Feicht, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest 3401* (1938).

[30] R. G. Keenan and L. T. Fairhall, *J. Ind. Hyg. Toxicol.*, *26*, 241 (1944).

beaker. Rinse the tube with water, adding the rinsings to the acid wash, and evaporate to a small volume. Store, if analysis is not to be performed immediately, in a glass-stoppered Pyrex cylinder.

The absorber liquid used in impingers or absorbers should be evaporated to a small volume after the addition of acid. If lead sulfate is deemed to be present, ammonium acetate should be added to aid in dissolving this compound. Nitric acid should not be used if alcohol is the absorbing liquid. Add either sulfuric acid or hydrochloric acid in place of the nitric acid.

Digest factory and street dusts with nitric acid (1:4) and leach with hot 25 per cent ammonium acetate solution. Filter off the extracts and use the combined filtrate for the analysis.

b. Lead Sulfide Method

The following method based on the precipitation of lead as the sulfide is a comparatively simple method and is easily adaptable to all types of sampling. It is limited, however, to those instances where most of the other metals of the insoluble sulfide group are absent or are present in negligible amounts and where lead is present in more than minute amounts. If the lead-bearing dust is caught on filters, papers, or cellulose materials, place these lead-bearing substances in a silica dish and ash at 550° C. Dissolve the ash in 10 ml. of water and 1 ml. of nitric acid. Filter, add a drop of phosphoric acid, and make the colorless filtrate alkaline with ammonia. The phosphate precipitate will contain practically all of the lead and the copper, if any is present, will remain in the filtrate as the complex ammonia compound. Filter, wash well and dissolve the precipitate in 5 ml. of dilute acetic acid. Make up to 50 ml. in a Nessler tube. Add 5 ml. of hydrogen sulfide solution and match the color with that of standard lead solutions treated in the same way. The lead sulfide precipitate may be stabilized by the use of solutions of arabic or ghatti by adding 1 ml. of a 5 per cent solution of gum ghatti or arabic to the solution in the Nessler tube before it is made to volume. The standards are treated the same way. The quantity of lead present is taken to be that of the closest standard.

c. Fairhall Method[31-35]

In this method, which is used for medium quantities of lead, the lead sample is ashed if necessary. The ash is dissolved and the lead is precipitated as the sulfide. If further separation is necessary, the sulfides are dissolved, separated in the usual manner, and the lead reprecipitated as the sulfide. The lead sulfide is redissolved and precipitated as the chromate.

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[31] L. T. Fairhall, *J. Ind. Hyg.*, *4*, 9 (1922–23).

[32] R. A. Kehoe, G. Edgar, F. Thamann, and L. Sanders, *J. Am. Med. Soc.*, *87*, 2081 (1926).

[33] R. A. Kehoe, F. Thamann, and J. Cholak, *J. Ind. Hyg.*, *15*, 257 (1933).

[34] T. V. Letonoff and J. G. Reinhold, *Ind. Eng. Chem., Anal. Ed.*, *12*, 280 (1940).

[35] J. J. Bloomfield and J. M. DallaValle, *U. S. Pub. Health Service, Bull. 217* (1935).

This precipitate is dissolved in turn in hydrochloric acid and the amount of lead present is ascertained by iodometric estimation with the addition of potassium iodide and titration with standard sodium thiosulfate solution, or it may be determined colorimetrically with s-diphenylcarbazide.

Procedure. Add 50 ml. of nitric acid (1:1) to the sample of lead dust collected with the aid of a Greenburg-Smith impinger or other impinger, or dissolve the lead specimen in the nitric acid. Evaporate the mixture to dryness on a hot plate. Care should be taken to avoid spattering. Digest the residue with 5 ml. of hydrochloric acid. Again evaporate the mixture to a volume of about 2 ml. and dilute to 100 ml. with water. In cases where the original residue is small the dilution at this point is halved. Neutralize the solution with 25 per cent sodium hydroxide until it is just alkaline to 4 drops of methyl orange indicator solution (0.5 g. in 100 ml. water), then add hydrochloric acid (1:2) until the faintest pink appears. Cool. Precipitate by passing in hydrogen sulfide gas for 1 hour. Allow to stand overnight. Filter on a 12.5-cm. Whatman No. 40 filter paper. Wash with freshly prepared hydrogen sulfide water to which has been added 0.1 per cent of its volume of hydrochloric acid. Wash the precipitate off the paper, using hot nitric acid (1:1), into the beaker in which the sulfide precipitation was made. Wash well with hot water. Wash down the sides of the beaker and the inside and outside of the hydrogen sulfide delivery tube, using hot nitric acid (1:1) followed by hot water. Remove the gassing tube. Evaporate the solution to a small volume on a hot plate and transfer to a 100 ml. beaker. Add 1 ml. of sulfuric acid, sp. gr. 1.84, and evaporate to sulfur trioxide fumes. Cool. Take up in 30 ml. of a mixture of 10 ml. of 95 per cent ethyl alcohol and 20 ml. of water. Allow to stand overnight.

Filter on a 7-cm. hard filter paper such as Munktell No. 1 F. Wash the beaker and the paper thoroughly, using a solution containing 1 ml. of sulfuric acid, sp. gr. 1.84, 10 ml. of 95 per cent alcohol and 20 ml. of water. Dissolve the precipitate off the paper into a 600-ml. beaker, using 10 ml. of hot 10 per cent ammonium acetate solution, followed by hot water. It is well to wash the beaker first and decant the solution through the filter. Dilute the filtrate to 300 ml. using cold water, add 2 drops of nitric acid, sp. gr. 1.42. Neutralize after adding 4 drops of methyl red, 1 g. in 100 ml. of 50 per cent ethyl alcohol, by adding 25 per cent sodium hyroxide solution to alkalinity, then hydrochloric acid (1:2) to a faint pink color. Add 1 ml. of hydrochloric acid in excess. Cool, precipitate the lead by passing hydrogen sulfide gas through the solution for 1 hour and allow to stand overnight.

Filter as described above. Dissolve the sulfides[36] from the paper with hot nitric acid (1:1), catching the solution and the washings in the beaker in which the sulfide precipitation was made. Wash the paper thoroughly with hot water and wash the sides of the beaker and the inside and outside of the hydrogen sulfide delivery tube with hot nitric acid (1:1) followed by hot water. Remove the gas-delivery tube. Evaporate the solution to a small volume, 1 to 2 ml., and transfer it to a 150-ml. beaker. Dilute to 80 ml. with cold water. Neutralize, after adding 4 drops of an aqueous solution of phenolphthalein, $^1/_2$ g. in 100 ml. of 1 per cent sodium hydroxide solution, using 25 per cent sodium hydroxide free from iron and aluminum. Make the solution alkaline. Add an excess of 5 drops of 25 per cent sodium hydroxide. Acidify with 5 per cent acetic acid till the pink color just disappears, and add 2 ml. of 5 per cent acetic acid in excess.

Bring the solution to a boil and precipitate the lead as chromate by adding 1 ml. of a 1 per cent potassium chromate solution. Place on a steam bath for 1 hour and allow to stand at 60°C. overnight. Filter on a Munktell No. 1 F filter paper. Wash the beaker and paper carefully and thoroughly with hot water to remove all possible traces of soluble chromate. Dissolve the precipitate from the paper into a 250-ml. volumetric flask containing 100 ml. of water, using 15 ml. of cold hydrochloric acid (1:2), followed by cold water. Wash the beaker and rod and decant through the paper.

Colorimetric Estimation with *s*-Diphenylcarbazide. In a 250-ml. volumetric flask prepare a standard containing sufficient potassium dichromate solution to be equivalent to 0.30 mg. of lead, precipitated as lead chromate. Add 100 ml. of water and 15 ml. of cold hydrochloric acid (1:2). To each of the samples and the standard add 2 ml. of a 1 per cent solution of *s*-diphenylcarbazide in glacial acetic acid. Make to volume and mix thoroughly. Estimate the lead in the samples by comparing the intensity of the pink colors, using a colorimeter.

An alternative method of preparing the lead standard to be used for matching against the unknown is the following[36]: Dissolve 0.142 g. of potassium dichromate in water and make up to 1 liter. One ml. of this solution is equivalent to 0.2 mg. of lead. Take 5 ml. of this solution, add 2 ml. of *s*-diphenylcarbazide, and make up to 1 liter. One ml. of this solution is equivalent to 0.001 mg. of lead.

Titrimetric Procedure. The use of *s*-diphenylcarbazide should be limited to the lower concentrations of lead. For larger amounts of lead, of the order of 10 mg., the titration method of Fairhall may be used, starting at the point of dissolving the precipitated lead chromate in hydrochloric acid, in which the lead chromate dissolves readily (see above). The lead may be estimated by adding an excess of potassium iodide and titrating the iodine liberated by the action of the chromic acid with 0.005 *N* sodium thiosulfate solution with the aid of a micro burette.

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[36] E. W. Krans and J. B. Ficklen, *J. Ind. Hyg.*, *13*, 140 (1931).

The following reactions proceed:

$$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2KNO_3$$

$$2PbCrO_4 + 16HCl + 6KI \rightarrow 2PbCl_2 + 2CrCl_3 + 6KCl + 3I_2 + 8H_2O$$

$$6Na_2S_2O_3 + 3I_2 \rightarrow 6NaI + 3Na_2S_4O_6$$

It is clear that 3 mols of thiosulfate are equivalent to 1 mol of lead chromate, in other words, 1 ml. of 0.005 *N* sodium thiosulfate is equivalent to 0.345 mg. of lead.

d. Dithizone Method

With the introduction by Fischer[37] of the dithizone method for the determination of lead, numerous variations of this method, among which may be mentioned the colorimetric, mixed color, and photometric modifications, have appeared. [21,38–50] These methods have the ability of detecting very small quantities of lead and are based on the formation of a red precipitate of a lead-dithizone complex, which is soluble in chloroform or carbon tetrachloride when an ammoniacal cyanide solution of dithizone is added to a solution containing lead.

Dithizone is the short name for diphenylthiocarbazone. It is the type of reagent which is best used for estimation of low concentrations. It forms green solutions in chloroform. The lead complex has a red color and is soluble in chloroform but is practically insoluble in dilute ammonia,

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[37] H. Fischer, *Z. angew. Chem.*, *42*, 1025 (1929).

[38] H. J. Wichmann, C. W. Murray, M. Harris, P. A. Clifford, J. H. Loughrey, and F. A. Vorhes, *J. Assoc. Official Agr. Chem.*, *17*, 108 (1934).

[39] F. A. Vorhes and P. A. Clifford, *J. Assoc. Official Agr. Chem.*, *17*, 130 (1934).

[40] O. B. Winter, H. M. Robinson, F. W. Lamb, and E. J. Miller, *Ind. Eng. Chem., Anal. Ed.*, *7*, 265 (1935).

[41] E. S. Wilkins, C. E. Willoughby, and E. O. Kraemer, *Ind. Eng. Chem., Anal. Ed.*, *7*, 33 (1935).

[42] C. E. Willoughby, E. S. Wilkins, and E. O. Kraemer, *Ind. Eng. Chem., Anal. Ed.*, *7*, 285 (1935).

[43] P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, *19*, 130 (1936).

[44] J. Cholak, D. M. Hubbard, R. R. McNary, and R. V. Story, *Ind. Eng. Chem., Anal. Ed.*, *9*, 488 (1937).

[45] D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, *9*, 493 (1937).

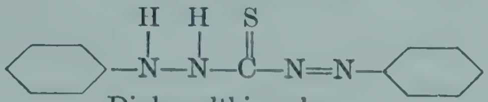
[46] H. Fischer and G. Leopoldi, *Z. anal. Chem.*, *119*, 161 (1940).

[47] K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, *11*, 400 (1939); *12*, 63 (1940).

[48] K. Bambach and R. K. Burkey, *Ind. Eng. Chem., Anal. Ed.*, *14*, 904 (1942).

[49] J. Schultz and M. A. Goldberg, *Ind. Eng. Chem., Anal. Ed.*, *15*, 555 (1943).

[50] E. N. Gómez, *Rev. Sanidad Asistencia Social (Venezuela)*, *11*, 477 (1946).



Diphenylthiocarbazone

whereas dithizone itself is soluble in this solvent. Upon these factors, the various methods for the isolation and subsequent determination of lead depend. The nature of the reaction that takes place between dithizone and a metallic salt and the structure of the resulting compound are not definitely known.

Interferences. Dithizone is not a specific reagent for lead, for it will form colored compounds with 14 other metals. Even in the presence of excess potassium cyanide, stannous tin, bismuth, and thallium interfere. Bismuth is eliminated as an interference by an extra dithizone extraction[51] from the lead solution before its final estimation by extracting a nitric acid solution of the two metals, which has been adjusted to a pH of 3.5, with a chloroform solution of dithizone. Table 9 shows the pH at which dithizone will extract different metal ions.

TABLE 9

Separations with Dithizone in Chloroform[52]

pH of aqueous solution	Metal ions extracted
Less than 2	Noble metals plus Hg
2–3	Cu, Bi, Sn^{++}
4–7	Zn, Cd, Pb, Tl, and all the above
7–10	All the above. Washing with 0.04 ammonia solution removes Sn^{++}. Addition of KCN leaves only Pb, Tl. or Bi, if not previously removed.

Both thallous thallium and stannous tin are converted to the thallic and stannic states during the evaporation step in the preparation of the sample by oxidation with nitric acid. This minimizes the possibility of their extraction by dithizone.

If interferences, such as tin, bismuth, or thallium, are likely to be present, it may be better to use the Wichmann-Clifford electrolytic method rather than any of the dithizone methods.

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[51] C. E. Willoughby, E. S. Wilkins, and E. O. Kraemer, *Ind. Eng. Chem., Anal. Ed.*, 7, 285 (1935).

[52] P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed.*, 9, 127 (1937).

Purification. Commercial diphenylthiocarbazone generally must be purified before use. Dissolve about 1 g. of the commercial reagent in 50 to 75 ml. of chloroform and filter if insoluble material remains. Shake out in a Jacobs-Singer separatory flask (Fig. 79), an apparatus designed to permit multiple extractions with a solvent of lighter specific gravity without disturbing the solvent layer of higher specific gravity, with four 100-ml. portions of metal-free, redistilled ammonium hydroxide solution (1:99). Dithizone passes into the aqueous layer to give an orange solution. Filter the aqueous extracts into a large separatory funnel through a pledget of cotton inserted in the stem of a funnel. Acidify slightly with dilute hydrochloric acid and extract the precipitated dithizone with two or three 20-ml. portions of chloroform. Combine the extracts in a Jacobs-Singer separatory flask and wash two or three times with water. Pour off into a beaker and evaporate the chloroform with gentle heat on the steam bath, avoiding spattering as the solution goes to dryness. Remove the last traces of moisture by heating for 1 hour at not over 50° C. in vacuo. Store the dry reagent in the dark in a tightly stoppered bottle. Make up the reagent solutions for extraction to contain approximately 100, 50, and 10 mg. per liter in redistilled chloroform. A stock solution of dithizone in chloroform containing 1 mg. per ml. will keep a long time and is convenient for use in making dilutions.

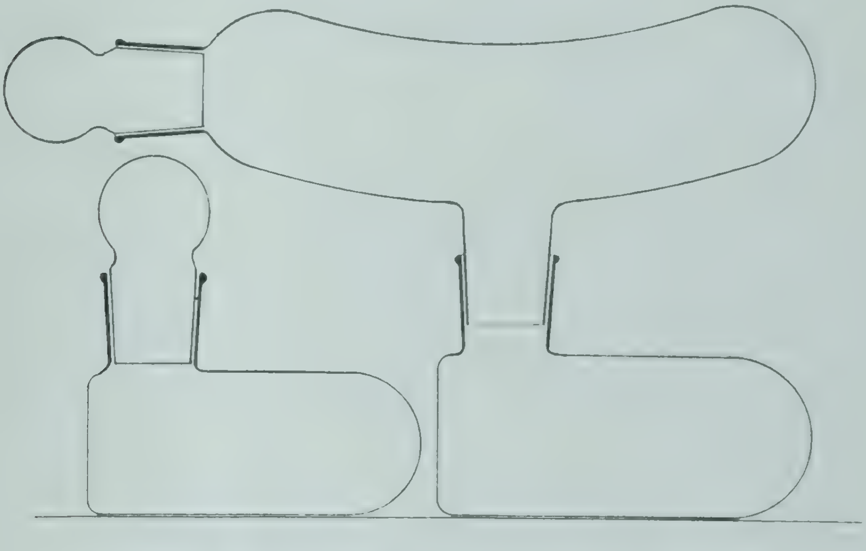

Fig. 79. Jacobs-Singer separatory flask.

Mixed-Color Photometric Method.[53] In this method lead is extracted with an excess of dithizone in chloroform solution but the excess is allowed to partition between the aqueous and chloroform phases and thus modify the color of the extract according to the relative amounts of lead and dithizone. Because, according to this proportion, a series of colors from red to green could be arranged with intermediate crimsons, purples, and blues, Clifford and Wichmann[54] termed this procedure a mixed-color method. If the extraction is made under definite conditions of volume and strength of dithizone solution and volume and strength and pH of aqueous fraction, the mixed color obtained is definite, reproducible, and, provided excess dithizone is present, depends only upon the amount of lead present.

The transmission spectra of the two components in the dithizone extract, namely, lead dithizonate and free dithizone, show a marked difference in their ability to absorb light of a wave length of 510 mμ, for the red-lead complex absorbs strongly and the free dithizone transmits freely. Consequently when the absorption of light of this wave length by the individuals of a standard color series, measured through suitable cell length, is determined photometrically, a practically linear relation is observed between the amounts of lead and the absorption coefficient.

Preparation of Reagents. (1) Ammonia-Cyanide Solution.—Add 75 ml. of concentrated ammonium hydroxide solution, sp. gr. 0.9, to 100 ml. of 10 per cent potassium cyanide solution and make up to 500 ml. with distilled water.

(2) Standard Dithizone Solution.—Dissolve 0.125 g. of purified dithizone (see page 000) in chloroform in a 250-ml. volumetric flask and complete to volume with chloroform. Each ml. is equivalent to 0.5 mg. of dithizone. The standard solutions listed in Table 9A may be prepared from this solution.

(3) Standard Lead Solutions.—Solution A.—Weigh out accurately 1.598 g. of recrystallized lead nitrate, $Pb(NO_3)_2$, and transfer to a 1-liter volumetric flask. Add 10 ml. of concentrated nitric acid and a few ml. of redistilled water to dissolve the salt. Make to volume with water and mix. This solution contains 1 mg. of lead per ml. It is stable and should be used as the standard lead stock solution. It should be discarded if any cloud or sediment appears. Solution B.—Dilute 100 ml. of solution A to 1 liter with water and then dilute 50 ml. of this to 500 ml. with nitric acid (1:1,000). One ml. of this solution contains 0.01 mg. of lead. This solution may be used for standardizing the dithizone in the 0–100 and 0–200 microgram lead ranges. Solution C.—Dilute 50 ml. of solution B to 500 ml. with nitric acid (1:1,000). This solution may be used for standardizing the dithizone for the 0–5, 0–10, 0–20, and 0–50 microgram lead ranges. Prepare solutions B and C as needed.

Standardization of Dithizone Solutions. The appropriate volumes and concentrations of solutions specified for the various ranges of lead content and the cell length are given in Table 9A on page 206.

Transfer with the aid of pipettes the required volumes of standard lead solution, 1 ml. of which equals some simple fraction or multiple of 1 microgram of lead, to a series of separatory funnels. Add sufficient nitric acid (1:1,000) to bring the volume to 50 ml. For so-called zero lead, use 50 ml. of nitric acid (1:1,000). Saturate each mixture with 2 ml. of chloroform by shaking. Allow to stand for a few minutes, swirling the funnel to carry down any globules of chloroform clinging to the side, and draw off the chloroform layer completely, being careful not to draw off any of the aqueous layer. Remove any chloroform in the stem with a pledget of cotton, or use filter paper. Add 10 ml. of the ammonia-cyanide mixture and mix. Immediately add the appropriate volume of dithizone solution as given in the table and shake for 1 minute. Allow to stand for 2 minutes and then filter the chloroform extract through lead-free filter paper (see page 197) inserted gently into the neck of a dry 50-ml. Pyrex Florence or similar flask in order to avoid loss of chloroform by evaporation. Rinse the proper absorption cell with a small volume of the dithizone extract and then fill the cell almost to the top of the vent with the extract. Set the cell in the trough of the photometer. Take the average of 5 or 10 readings, which seldom vary more than 2 mm. Plot scale readings against micrograms of lead on a large scale graph.

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[53] Morris B. Jacobs, in A. Cantarow and M. Trumper, *Lead Poisoning*, Williams & Wilkins, Baltimore, 1944.

[54] P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, *19*. 130 (1936).

TABLE 9A

Dithizone Concentrations and Cell Lengths for Various Lead Ranges

Lead ranges, µg.	Dithizone concentration, mg./liter	Volume, ml.	Cell length, inches
0–5	4	5	2
0–10	4	10	2
0–20	8	10	1
0–50	8	25	1
0–100	10	30	$^1/_2$
0–200	20	30	$^1/_2$

Procedure.[55] Prepare the sample as previously directed or, if organic matter is present, evaporate to dryness on a steam bath or hot plate. Transfer the dish to an electric muffle oven and gradually raise the temperature to 500° C. Ash overnight at this temperature. Remove the dish, cool, wash down the sides with 2 ml. of concentrated nitric acid, and evaporate to dryness as before. Replace in the muffle furnace and heat for about 30 minutes or until a white ash is obtained. Remove the dish, cool, add 10 ml. of concentrated hydrochloric acid, and evaporate to dryness on a steam bath or hot plate. Add another 10-ml. portion of concentrated hydrochloric acid and again evaporate to dryness. Remove the dish and while it is still hot add 2 ml. of hydrochloric acid and about 20 ml. of hot water to dissolve the ash completely. Transfer to a 250-ml. separatory funnel. Add 10 ml. of 50 per cent citric acid solution to the dish, add a small quantity of hot water, swirl gently, and add to the separatory funnel. Rinse the dish three times with hot water and add the washings to the funnel. Mix the contents of the separatory funnel and add 2 to 3 drops of metacresol purple indicator solution. Adjust the pH to 8.5 with concentrated ammonium hydroxide with the aid of a burette and cool.

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[55] V. A. Gant, *Lead Poisoning*, Industrial Health, Chicago, 1939.

Generally 7 to 8 ml. is needed. Add 5 ml. of 10 per cent potassium cyanide solution to the dish, rinse into the separatory funnel with water, and mix. The total volume should be about 100 to 125 ml. Add 5-ml. portions of the dithizone solution (20 mg. dithizone per liter of chloroform), shaking between additions until the chloroform extract assumes a purple color. Allow to stand for a few minutes and swirl to shake down the chloroform globules. Draw off the chloroform phase into a 125-ml. separatory funnel containing 50 ml. of nitric acid (1:1,000) but permit a drop or two of chloroform to remain in the first funnel. Repeat the extraction of the aqueous phase with 20 ml. of the dithizone solution and combine the chloroform extracts. Shake for 1 minute to strip the lead from the dithizone complex. Discard all but 2 to 3 ml. of the dithizone solution, dilute with 2 to 3 ml. of chloroform and shake for 2 minutes. If the dithizone retains its original green color, bismuth is absent. A trace of bismuth will give the dithizone solution a dirty purple or iridescent blue color, a larger amount of this metal yields a yellowish brown. If bismuth is present, extract repeatedly with excess dithizone, shaking for 2 minutes between extractions until the dithizone retains its original color. Discard the dithizone layer and wash the aqueous portion with successive 2- to 3-ml. portions of chloroform until free from dithizone. Shake down globules of chloroform and allow to stand for a few minutes. Draw off the chloroform layer completely, being careful not to draw off any of the aqueous layer.

Add 10 ml. of the ammonia-cyanide mixture and mix. Add the appropriate volume of standardized dithizone solution (see Table 9A) and shake for 1 minute. Allow to stand for 2 minutes and filter through specially prepared filter papers inserted directly into the neck of a 50-ml. Pyrex Florence or similar flask. The lead-free filter papers are prepared by soaking overnight in nitric acid (1:100) and then washing with large volumes of water with the aid of a Büchner funnel until free of acid. Rinse out the proper cell with a small amount of the filtered extract and fill it almost to the top. Determine the absorption coefficient, using the standardized dithizone with the same cell used in making the standard curve, and read the amount of lead from the curve or calculate from the factor of the dithizone solution as detailed by the A. O. A. C.[56]

Simple color matching may be made without the use of a photometer by making a series of 10 standards as detailed on page 205, but drawing off the dithizone layers into a series of tubes, vials, or Nessler tube. The unknown is treated in a similar way and drawn off into a similar tube or vial. View longitudinally for ranges up to 20 micrograms in the flat-bottomed vials and transversely for higher ranges in Nessler tubes. If the range is exceeded, use a smaller aliquot, or re-extract with nitric acid reagent and make standards covering a higher range.

Bambach-Burkey Modification.[57] *Preparation of Reagents.* (1) Ammonium Citrate Solution. Dissolve 400 g. of citric acid in water and add sufficient ammonium hydroxide solution to make the solution alkaline to phenol red. Dilute the solution to 1 liter with water and extract with successive portions of a chloroform solution of dithizone until the dithizone solution retains its original green color. Remove the excess dithizone by repeated washes with chloroform. Sodium citrate may be used in place of the citric acid and ammonium hydroxide. It should be purified in the same way.

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[56] *Methods Assoc. Official Agr. Chem.,* 1940.

[57] K. Bambach and R. E. Burkey, *Ind. Eng. Chem., Anal. Ed., 14,* 904 (1942).

(2) Hydroxylamine Hydrochloride Solution. Dissolve 20 g. of hydroxylamine hydrochloride, $NH_2OH.HCl$, in sufficient water to make 65 ml. of solution. Add a few drops of metacresol purple indicator solution. Add concentrated ammonium hydroxide solution until a yellow color is obtained. Add sufficient 4 per cent aqueous sodium diethyldithiocarbamate solution to combine with all the lead and most of the other metals present and leave an excess of reagent. Extract the excess and the metallorganic complexes with chloroform. Test for complete removal by shaking a portion of the chloroform extract with a dilute aqueous solution of a copper salt. Add distilled hydrochloric acid until the indicator turns pink, and complete the volume to 100 ml. with water.

(3) Potassium Cyanide Solution. Dissolve 50 g. of potassium cyanide in sufficient water to make 100 ml. Extract repeatedly with a chloroform solution of dithizone until all the lead has been removed. Excess dithizone in the aqueous layer can be removed by successive washes with chloroform. Dilute with water to give a 10 per cent solution.

(4) Dithizone Extraction Solution. Shake 1 liter of chloroform with 100 ml. of water containing about 0.5 g. of hydoxylamine hydrochloride, which has been made alkaline to phenol red with ammonium hydroxide. Drain off the chloroform and dissolve 30 mg. of dithizone in it. Add 5 ml. of alcohol to this solution if it is to be kept for several days. Shake the quantity of dithizone that is to be used with 100 ml. of hydrochloric acid (1:100) just before use.

(5) Standard Dithizone Solutions. Prepare chloroform as directed in the preceding paragraph. Filter the chloroform through dry filter paper into a Pyrex bottle equipped with a glass stopper and shield from light with wrapping paper or a wooden box. Dissolve dithizone in the following ratios in the chloroform: 5 mg. per liter for the 0–10-microgram range of lead; 10 mg. per liter for the 0–50-microgram range; and 20 mg. per liter for the 0–100-microgram range. Add 5 ml. of asbolute alcohol per liter and hold in a refrigerator.

(6) Buffer Solution. Transfer 9.1 ml. of reagent nitric acid to a 1-liter volumetric flask and dilute to about 500 ml. with water. Add bromophenol blue indicator and adjust the pH to 3.4 with ammonium hydroxide solution. Add 50 ml. of double-strength Clark and Lubs potassium acid phthalate-hydrochloric acid buffer (pH 3.4) prepared by diluting 50 ml. of 0.2 *M* potassium acid phthalate and 9.95 ml. of 0.2 *M* hydrochloric acid to 100 ml., and dilute the entire mixture to 1 liter.

Procedure. Transfer 15 ml. of ammonium citrate solution to a separatory funnel. Add the proper aliquot of the sample being analyzed and 1 ml. of hydroxylamine hydrochloride solution, mix, and make the mixture alkaline to phenol red with ammonium hydroxide solution. Add 5 ml. of potassium cyanide solution.

Start the extraction of lead with 5 ml. of dithizone extraction solution and note the color to assist in choosing the proper standard dithizone solution to be used later. Less than 10 micrograms of lead is indicated by a greenish-blue color. Add another 5-ml. portion of dithizone extraction solution. Shake, allow to separate, and again note the color to ascertain whether the quantity of lead is greater than 50 or 100 micrograms. Drain off the dithizone and continue the extraction with successive 5-ml. portions of dithizone solutions, noting the color in each instance before draining, until all of the lead is extracted. Wash the combined dithizone extracts with 50 ml. of water, and wash the water with 5 ml. of chloroform. This wash should be green in color; if it is not, the presence of more lead or of zinc is indicated. Add a drop of potassium cyanide solution and shake the funnel again. If the chloroform layer does not become green, the water should be washed at least once with dithizone extraction solution. Add all chloroform washings to the dithizone extract and discard the aqueous layer. Strip the lead from the dithizone extract by shaking with 50 ml. of buffer solution (pH 3.4); if the dithizone solution does not return to its original color, bismuth is present. Drain the dithizone solution from the separatory funnel. If more than 100 micrograms of lead is indicated, discard an aliquot portion of the buffer solution, sufficient to bring the quantity within the 100 microgram range, and make up to 50 ml. again with buffer solution. If bismuth is indicated, shake the buffer solution with one 5-ml. portion of dithizone solution. Drain, add 5 ml. of chloroform, and shake. Allow to stand until the supernatant drop of chloroform evaporates and draw off as much chloroform as possible without permitting any of the aqueous phase to enter the bore of the stopcock.

Estimation of Lead. Do not allow direct sunlight to strike the solutions. Add the proper standard dithizone solution, described above, to the separatory funnel containing the lead in the buffer solution, using 10 ml. of the 0–10-microgram solution and 25 ml. of the other solutions. Add 7 ml. of ammonia-cyanide mixture and shake immediately for 1 minute. Do not release the pressure that is developed through the stopcock, but permit the gases to escape through the stopper. Flush the stem of the separatory funnel with 2 ml. of the 0–10-microgram standard and with 10 ml. of the other standards and dry the stem. Rinse the photometer cells twice with the test solution, but since the 0–10-microgram cell will hold the entire 8 ml. remaining of the test solution, these cells should be cleaned and dried with acetone after each determination. Use a 5-cm. (2-inch) cell for the 0–10-microgram solution; a 1.25-cm. (0.5-inch) cell for the 100-microgram solution; and a 2.5 (1-inch) cell for the 0–50-microgram solution. Read in a photometer and refer to a calibration curve prepared as directed below.

Prepare a fresh lead standard by taking an aliquot of the lead standard solutions prepared as directed above and adjust the pH to 3.4 by addition of dilute ammonium hydroxide. Add the proper amount of 3.4-pH buffer and dilute the mixture to a known volume. Add measured quantities of this prepared standard lead solution to separatory funnels, adjust the volume to 50 ml. with additional buffer solution, and add the dithizone solution to be standardized. Read in a photometer as described above and prepare a calibration curve.

One-Color Extraction Method.[58] In this method the lead is extracted with a small excess of dithizone in chloroform solution and the excess dithizone is removed from the combined extracts by washing with dilute ammonia-potassium cyanide solution. The amount of lead in the extract is then estimated colorimetrically by a comparison of the red color of the lead-dithizone complex.

Preparation of Reagents. (1) Prepare a 5 per cent solution of ammonium citrate from citric acid by the addition of ammonium hydroxide until just alkaline to litmus paper.

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[58] G. C. Harrold, S. F. Meek, and F. R. Holden, *J. Ind. Hyg.*, *18*, 725 (1936).

(2) Lead Extractive Solution. Mix 15 ml. of 10 per cent potassium cyanide solution, 10 g. of potassium cyanide dissolved in water and made up to 100 ml., and 20 ml. of ammonium citrate solution with 53 ml. of concentrated ammonium hydroxide solution, sp. gr. 0.9, and then add 450 ml. of water. This solution is used to neutralize the excess nitric acid and provide the proper pH of from 9.5 to 10.

(3) Dithizone Extractive Solution. Dilute 5 ml. of 10 per cent potassium cyanide solution and 15 ml. of concentrated ammonium hydroxide to 500 ml. with water.

(4) Standard Lead Solution. Dissolve 1.598 g. of recrystallized lead nitrate in 0.1 per cent nitric acid and make up to 1 liter with this solvent. One ml. of this solution contains 1 mg. of lead. Dilute 10 ml. of this solution to 1 liter. One ml. of this dilution equals 0.01 mg. of lead.

Procedure. Collect the sample either with 10 ml. of nitric acid or in water as has been previously explained. If collected in water, add the same quantity, that is, exactly 10 ml. of concentrated nitric acid, or the additional amount of acid if a lesser quantity was used in the collector, after collection. Boil the sample in the original sampling vessel until the volume is less than 90 ml. After cooling, transfer to a 100-ml. volumetric flask. Wash the sampling flask with two 5-ml. portions of water and add this wash water to the volumetric flask. Then dilute to the mark with water. Remove a 5-ml. aliquot containing approximately 0.5 ml. of concentrated nitric acid. It is important to add exactly 10 ml. of nitric acid and no more. Too little acid will cause the destruction of the dithizone reagent. Too great an amount will lower the pH below 9.7, which is the alkalinity to which the lead extractive solution has been adjusted. This was shown to be the optimum pH by Clifford and Wichmann.[59] The reagents have been adjusted to care for all the commonly interfering metallic ions, but the procedure must nevertheless be closely followed.

Place 15 ml. of the lead extractive solution containing the potassium cyanide, ammonium citrate, ammonium hydroxide, and water into a Squibb or pear-shaped separatory funnel. Add the 5-ml. aliquot of the unknown with the aid of a standard pipette. Add dithizone solution, 25 mg. dithizone per liter of chloroform, from a semi-micro burette in 0.3-ml. portions, shaking the separatory funnel after each addition until a slight purple tinge is noticed in the chloroform layer. This purple tinge shows that uncombined dithizone is now present. The dithizone in the chloroform layer turns a bright cherry red when shaken with solutions containing lead. Add chloroform from a burette in sufficient amount so that the total of dithizone-chloroform solution and chloroform is equal to exactly 10 ml. Shake for not over 10 seconds. Allow the layers to separate. Drain the chloroform layer into another Squibb separatory funnel containing 20 ml. of the dithizone extractive solution, consisting of potassium cyanide and ammonium hydroxide. Shake the chloroform layer with the 20 ml. of dithizone extractive solution, if too great an excess of dithizone has been added. Repeat if necessary to remove the excess dithizone. It has been shown that two extractions are usually sufficient to remove any excess. The color of the resulting chloroform solution is a bright, clear cherry red. The drop at the top of the aqueous layer may be brought down to the rest of the chloroform by repeatedly tapping and shaking with a slight rocking motion.Transfer the chloroform layer into a test tube or comparator tube, first wiping the inside of the stem of the separatory funnel with a cotton swab or pipe cleaner to remove moisture. The test tube or comparator tube should then be stoppered.

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[59] P. A. Clifford and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, *19*, 130 (1936).

Three standard solutions containing 0.005, 0.01, and 0.015 mg. of lead, respectively, are made at the same time that the unknown is prepared for analysis. These standards, after the lead extraction and the removal of excess dithizone, are placed in tubes similar to those used for the unknown. By placing the unknown sample between the two standards that are nearest the unknown in shade, and holding it up in front of a standard source of white light, one is able to determine the lead content within 0.001 mg. This does not hold when more than 0.1 mg. of lead is present in the sample taken for analysis. Best results are obtained when the aliquot taken contains less than 0.04 mg. of lead.

To prepare the 0.005-mg. standard, add 5 ml. of the dilute lead nitrate standard solution to 40 ml. of water and 5 ml. of concentrated nitric acid. Then, after this solution has been thoroughly mixed, take a 5-ml. aliquot and treat it exactly as has been described for the unknown. Use proportionately larger amounts of the dilute lead standard solution for the other standard comparison solutions.

To make up standards for comparison containing 0.045 mg. or more of lead, use the concentrated lead nitrate solution containing 1.0 mg. of lead per ml. Thus, for making an 0.07 mg. standard, add 0.7 ml. of the concentrated lead nitrate standard solution to 5 ml. of nitric acid and dilute to 50 ml. with water. Take 5 ml. of this as an aliquot for analysis. The resultant pH is between 9.5 and 10 under conditions as stated.

When large amounts of iron[60] are present in samples analyzed for lead by the colorimetric dithizone method, fading will occur unless a small amount of hydroxylamine hydrochloride is present as an inhibitor.

Add 2 to 4 drops of a saturated aqueous solution of hydroxylamine hydrochloride to each sample and standard prior to the addition of dithizone. When 200 to 300 times as much iron as lead is present, extract the lead with an excess quantity of very strong dithizone solution (approximately 100 mg. per liter) and then strip the excess with the dithizone extractive solution. The final color is developed after adding 2 drops of hydroxylamine hydrochloride to the solution, which is brought to a pH of 9.5 to 10.0 by the addition of a known quantity of standard dithizone solution, as in the procedure above.

Titrimetric Method. In this method[61,62] the lead is separated from a given solution by means of dithizone and the resulting lead-dithizone complex is then isolated. The latter is freed of lead by washing with acid. The chloroform solution of dithizone remaining is mixed with some dilute cyanide solution, which removes most of the dithizone from the chloroform, imparting a brown color to the aqueous layer. A lead solution is added from a burette to this mixture until all the dithizone has been reconverted to lead dithizonate, as indicated by (1) the disappearance of the brown color in the aqueous layer, and (2) the absence of a red color when the aqueous layer is mixed with chloroform and additional lead solution. As the final titration is carried out directly with a known standard lead solution, it eliminates the necessity for special precautions in the handling of the dithizone.

Preparation of Reagents. (1) Dithizone Solution. Dissolve 40 mg. of dithizone in 400 ml. of chloroform and filter into a 500-ml. Pyrex separatory funnel. Add 50 ml. of water containing 2 ml. of 25 per cent hydroxylamine hydrochloride solution and shake. Keep in a cool dark place and withdraw the chloroform solution as needed. The acid aqueous layer not only prevents the oxidation of the dithizone but also extracts any lead that might be present.

(2) Potassium Cyanide Solution, 0.5 per cent. Prepare when needed

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[60] G. C. Harrold, S. F. Meek, and F. R. Holden, *J. Ind. Hyg. Toxicol.*, *20*, 589 (1938).

[61] M. K. Horwitt and G. R. Cowgill, *J. Biol. Chem.*, *119*, 553 (1937).

[62] S. Moskowitz and W. J. Burke, *N. Y. State Ind. Bull.*, *17*, 492 (1938); *J. Ind. Hyg Toxicol.*, *20*, 457 (1938).

by diluting 25 ml. of a freshly prepared 10 per cent solution of potassium cyanide to 500 ml. with water. It is important that this solution be lead-free. To insure this, place 100 ml. of 10 per cent potassium cyanide solution into a separatory funnel and extract with 2 ml. of chloroform containing 2 drops of dithizone solution. If a pink color appears in the chloroform layer, withdraw it and repeat the extraction until the chloroform layer is colorless. The slight excess of dithizone which remains in the 10 per cent potassium cyanide solution is insignificant because the amounts which remain after dilution to form the 0.5 per cent solution of potassium cyanide are not detectable.

(3) Standard Lead Solution. Dissolve 1.598 g. of recrystallized lead nitrate with the aid of 1 ml. of nitric acid in a volumetric flask and dilute to 100 ml. This solution, which contains 10 mg. of lead per ml., is stable. By diluting 10 ml. of this solution to 100 ml. and then in turn diluting 10 ml. of the latter to 1 liter, a solution containing 0.01 mg. of lead per ml. is prepared.

(4) Sodium Citrate, 20 per cent. To 800 ml. of this solution add 8 ml. of 10 per cent potassium cyanide and extract in a 1-liter separatory funnel with 15-ml. portions of dithizone solution until the citrate mixture is free of lead. Wash twice with 25-ml. portions of chloroform, acidify with 4 ml. of 20 per cent hydrochloric acid, and complete the extraction of the excess dithizone with 20-ml. portions of chloroform.

Procedure. Wash the sample of dust collected from the air or the ash from other type collections into a 250- or 400-ml. Pyrex beaker with the aid of about 10 ml. of hot concentrated nitric acid. Evaporate the contents of the beaker just to dryness. Place 15 ml. of hydrochloric acid (1:1) in the beaker and heat to boiling. Wash the mixture into a 100-ml. volumetric flask with small portions of hot water. Wash the beaker with a mixture consisting of 10 ml. of 20 per cent sodium citrate solution and 3 ml. of ammonium hydroxide solution (1:1). Warm and transfer to the volumetric flask. Wash with 2 or 3 small portions of hot water and add the washings to the contents of the flask. Cool to room temperature, add 1 ml. of 25 per cent hydroxylamine hydrochloride solution and 2 drops of phenol red. Adjust the pH of the solution to 8.0 by the addition of ammonium hydroxide solution (1:1). Cool the solution again to room temperature and make up to volume. After thorough mixing, proper aliquots may be removed and transferred by means of pipettes to separatory funnels for analysis. Dilute to 75 ml.

If the lead-bearing material contains organic matter, place the specimen in a silica evaporating dish, evaporate to dryness, if necessary, dry, and ignite in a muffle oven at about 475° C. Remove the dish from the muffle and if a clean ash is not obtained, add 2 ml. of nitric acid, evaporate to dryness, and ignite again in the muffle. Place the dish on a hot plate, carefully add 15 ml. of 20 per cent hydrochloric acid (1:1), and heat until the ash is dissolved. Wash the contents into a 125-ml. separatory funnel with about 20 ml. of hot water. Add 10 ml. of 20 per cent sodium citrate solution and 3 ml. of ammonium hydroxide to the silica dish, mix, and transfer to the separatory funnel with enough water to make a total volume of about 75 ml. Cool, add 1 ml. of 25 per cent hydroxylamine hydrochloride solution, 1 drop of phenol red, and bring to a pH 8.0 with ammonium hydroxide delivered from a Pyrex burette. Cool.

Add 0.5 ml. of 10 per cent potassium cyanide solution drop by drop, shaking between additions, and immediately extract with 0.5 ml. of dithizone solution and 4 ml. of chloroform. If, after shaking, the chloroform layer does not contain a noticeable excess of uncombined dithizone, add 0.5-ml. portions of dithizone solution, shaking between additions until the green excess becomes evident. Transfer the chloroform phase to another separatory funnel and repeat the extraction of the aqueous phase twice with 0.2-ml. portions of dithizone in 2 ml. of chloroform. To the combined chloroform solutions add an amount of 0.5 per cent potassium cyanide equal to 1.5 times the volume of the chloroform solution and shake for 10 seconds. Transfer the chloroform layer to another separatory funnel and wash the aqueous cyanide solution with 1 ml. of chloroform. Combine the chloroform solutions and again extract with 1.5 volumes of 0.5 per cent potassium cyanide solution. The extraction with cyanide removes the uncombined dithizone unless a very large excess has been used, in which case the extraction with 0.5 per cent potassium cyanide solution is continued until the absence of color in the aqueous phase indicates that the dithizone excess has been removed.

Remove any lead which may have dissolved in the aqueous layer by extraction with 2 ml. of chloroform. Separate the lead from the red dithizone complex by shaking for 15 seconds with 2 volumes of 1.0 per cent hydrochloric acid. Withdraw the green chloroform layer and then extract the acid aqueous solution with 1 ml. of chloroform to recover the last traces of dithizone. Combine the chloroform fractions.

Add to the dithizone solution 0.5 of its volume of 0.5 per cent potassium cyanide and shake. Most of the dithizone goes into the aqueous layer, giving that mixture a brown color. Add the standard lead solution (0.01 mg. per ml.) from a burette a drop at a time, shaking between additions.

until only a very faint color remains in the aqueous layer. This is evidence that practically all of the dithizone has combined with lead and gone into the chloroform phase. Discard the red chloroform layer and wash the aqueous layer with chloroform, 2 ml. at a time, until the chloroform layer remains colorless after shaking. Add 1 or 2 drops of the lead solution and shake for 5 seconds. Draw off the pink chloroform solution and continue the extraction with 2-ml. portions of chloroform plus 1 or 2 drops of lead solution until further addition of lead gives no pink color to the chloroform solution after shaking. The end point is a slight pink in the chloroform solution; extraction with 1 drop more results in a colorless solution. In order to facilitate the titration, a solution of the lead-dithizone complex containing a small amount of the order of 1 or 2 drops of the lead solution in 2 ml. of chloroform is kept for comparison. When the color obtained after an addition of lead solution is less than that given by 1 drop of the lead solution, the end point has been attained. It is suggested that the analyst unaccustomed to this analysis add 2 drops (equivalent to about 0.0006 mg.) at a time until his eyes become accustomed to the change.

For ease of manipulation, the aliquot taken for analysis should contain less than 0.050 mg. of lead. A rough estimate of the quantity of lead in the aliquot can be made by observing the volume of dithizone solution used to produce an excess. One ml. of dithizone solution will combine with approximately 0.040 mg. of lead.

The number of ml. of standard lead solution used in the titration multiplied by 0.01 gives the quantity of lead in mg. in the aliquot taken for analysis.

e. Wichmann-Clifford Method[63,64]

This method is based on the electrolytic separation of lead as the peroxide and its titration by iodometric means. The lead is deposited on the anodic, positive pole, by the use of a low electric current. Tin, antimony, bismuth, and manganese interfere with the deposition and must, therefore, be removed. Samples are ashed, if necessary, and precipitated with hydrogen sulfide, using copper as a collector for the lead. The sulfides are filtered, washed with hot polysulfide solution, and finally with sodium sulfate solution. The lead and copper sulfides remaining are then dissolved in hot nitric acid, neutralized with ammonium hydroxide, and made up to 2 per cent acid with nitric acid. Potassium dichromate solution is added, the solution heated and electrolyzed, and the lead deposited as the peroxide, PbO_2. It is then washed thoroughly and removed from the anode with a sodium acetate

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[63] H. J. Wichmann and P. A. Clifford, *J. Assoc. Official Agr. Chem., 17,* 123 (1934).

[64] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products,* Van Nostrand. New York, 1945.

acidic solution. Potassium iodide is added and the liberated iodine titrated with 0.001 *N* sodium thiosulfate solution, using starch as an indicator.

Reagents. (1) Polysulfide Solution. Dissolve 480 g. of sodium sulfide, $Na_2S.9H_2O$ and 40 g. of sodium hydroxide, NaOH, in water. Add 16 g. of powdered sulfur, shake until the sulfur dissolves, filter, and dilute to 1 liter.

(2) Sodium Thiosulfate Solution. Dissolve 24.85 g. of sodium thiosulfate, $Na_2S_2O_3.5H_2O$, in 1 liter of carbon dioxide-free water. Protect the solution with a soda lime tube and thiosulfate trap and allow it to stand for about 2 weeks. Prepare an approximately 0.001 *N* solution by diluting this reagent with carbon dioxide-free water in the ratio of 1:100. Standardize this dilute solution by running known quantities of lead nitrate of the order of 2 to 4 mg. or 0.2 to 0.5 mg., respectively. Prepare the dilute solutions at least every other day, but standardize the solution daily.

(3) Standard Lead Solution. Lead nitrate may be recrystallized from water to obtain a reasonably pure salt. Dissolve 20 to 50 g. of C. P. lead nitrate in a minimum amount of hot water and cool with stirring. Filter the crystals with suction on a small Büchner funnel, redissolve, and repeat the crystallization. Dry the crystals at 100–110° C. to constant weight. Cool in a desiccator and preserve in a tightly stoppered bottle. The product has no water of crystallization and is not appreciably hygroscopic. Prepare a solution containing 10 mg. of lead per ml. in about 1 per cent nitric acid and from this solution make weaker dilutions as needed. Because lead tends to precipitate, probably as a silicate, from very dilute solutions, the weaker dilutions should not be used over long periods of time.

Method. Prepare an ash of an adequate amount of material as described in previous sections. Add 30 ml. of hydrochloric acid (1:1) and heat to boiling. Filter and wash with hot water into a 250-ml. beaker. If a large quantity of unburnt carbon remains, return the residue and filter into the casserole or ashing dish and re-ash. Rinse the ashing dish and then extract the residue with 20 ml. of hydrochloric-citric acid mixture (1:1), the hydrochloric acid containing 20 per cent citric acid. Filter the extract into the same beaker. Place a few pellets of sodium hydroxide in the ashing dish and add 1 to 2 ml. of hot water. Allow the syrupy solution to wet the inside of the dish completely and heat until nearly dry. Take up the residue in a little water and run the alkaline wash directly into the filtrate, so as not to redissolve the silica that may be on the filter. Finally rinse the casserole or ashing dish with a few ml. of hot hydrochloric acid (1:1) followed by one to two washings of hot water.

If the sample was trapped in water or nitric acid solution, an aliquot should be taken to dryness in a suitable dish and then redissolved in hydrochloric acid (1:1). If necessary, the remainder of the drastic dissolving treatment with hydrochloric-citric acid and with sodium hydroxide may be made.

Cool the filtrate. Add 1 ml. of thymol blue (40 mg. of thymol blue indicator in 100 ml. of water) and add ammonium hydroxide from a burette until the color changes from reddish orange to a distinct yellow, at which point the pH is 2.8. To obtain a more accurate pH, add 4 drops of bromophenol blue (40 mg. bromophenol blue indicator in 100 ml. of water) and continue adding ammonium hydroxide until the color changes through olive green to a purple color, which is obtained at a pH of 3.8 or greater. The pH range, for the precipitation of lead sulfide, without coprecipitation of iron sulfide, is from 2.5 to 3.4. The color of the solution using these indicators is an incipient purple to olive green at this pH. Adjustment to the correct pH point must always be made from the acid side to prevent precipitation of alkaline earths, aluminum, iron hydrates, and phosphates.

Add 5 ml. of copper sulfate solution (10 g. of $CuSO_4.5H_2O$ dissolved in water and made up to 1 liter) and pass hydrogen sulfide into the cold solution for 3 minutes. Filter the sulfides immediately, preferably on a Jena-glass filter No. 11G, or equivalent Pyrex type. This type of sintered-glass filter may be cleaned with sulfuric acid, hydrochloric acid, or 10 per cent sodium hydroxide solution, followed by reverse flushing with hot water. A light mat of asbestos should cover the filter, to prevent clogging the pores of the filter. Dissolve any tin, antimony, or arsenic sulfides from the filter with five applications of 5 ml. each of warm polysulfide reagent, prepared as directed above. Wash the filter four times with 3 per cent sodium sulfate solution (3 g. of anhydrous Na_2SO_4 in 100 ml. of water).

Dissolve the sulfides retained with 5 ml. of hot nitric acid, catching the filtrate in a beaker mounted under the funnel, and rinse the filter thoroughly with hot water. Boil the solution until the sulfur is coagulated or oxidized. Neutralize the solution with ammonium hydroxide, add 2 ml. of concentrated nitric acid, and bring the volume to 100 ml. with water. These volumes are preferable when electrodes 1 by $^5/_{16}$ by 5 inches overall are used.

The conditions of electrolysis should be carefully regulated. Low acidity, constant speed of the revolving anode, constant elevated temperature, and low current density counteract the interference of phosphates, arsenic, and traces of chlorides and insure the complete deposition of small amounts of lead as the peroxide. Low acidities are essential for the amounts of lead usually estimated by this method, in the order of 0 to 10 mg. of lead. Higher acidities may be used for larger quantities of the metal. Low current densities are also essential. High acidities and high current densities promote the production of nitrites, which seriously interfere with the determination of small amounts of lead.

Before electrolyzing, heat the anode to red heat in a Bunsen flame. Heat the solution to about 75° C. over a gas flame and then add 1 ml. of potassium dichromate solution (100 g. of $K_2Cr_2O_7$ dissolved in water and made up to 1 liter) to suppress nitrite formation. Start the current and adjust to 75 to 80 milliamperes and electrolyze, while the anode is revolving at 450 r. p. m. Maintain the temperature between 70 and 80° C. Electrolytic apparatus designed so that all the conditions specified may be controlled are commercially available. One of these is illustrated in Figure 80. For equipment necessary to build a laboratory apparatus see Wichmann and Clifford.[65]

The time of electrolysis may vary according to conditions. Efficient stirring shortens the time so that with proper equipment 15 minutes is usually long enough. If the speed is not great enough, stir the solution well, and if more than 5 to 10 mg. of lead is expected, increase the time to 20–25 minutes.

If possible remove the acid by siphoning, at the same time adding water to keep the level of the solution above the deposit on the anode. The acid is entirely removed only when the current drops to zero. Remove the anode from the chuck and rinse it again with water.

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[65] H. J. Wichmann and P. A. Clifford, *J. Assoc. Official Agr. Chem.*, *17*, 123 (1934).

Place the anode in a small flat-bottom tube, add 5 ml. of stripping solution, consisting of 5 ml. of acetate mixture (to 20 ml. of a saturated sodium acetate solution add 10 ml. of glacial acetic acid and make up to 100 ml. with water), and 1 ml. of potassium iodide solution, 2 g. of KI dissolved in water and made up to 100 ml. Add a few drops of starch solution and titrate the liberated iodine with 0.001 *N* thiosulfate solution, using a micro burette. Using the electrode as a stirrer, sight through the entire depth of liquid to detect the delicate end point, which is reached when the last faint starch iodine color just disappears. A white opal base support aids in ascertaining the end point. If the quantity of lead is high, of the order of 1 to 5 mg., which may be noted from the dark appearance of the anode, use a double quantity of the reagents and 0.005 *N* thiosulfate solution. The starch solution should not be added until the end point is approached. This may be detected when the yellow color of the solution begins to disappear. Calculate the quantity of lead determined from the factor of the thiosulfate, previously standardized against pure lead nitrate. The reagents used should be as pure as possible. Every precaution should be taken to have clean apparatus. As a precautionary measure, it is wise to run blanks with every series of determinations.

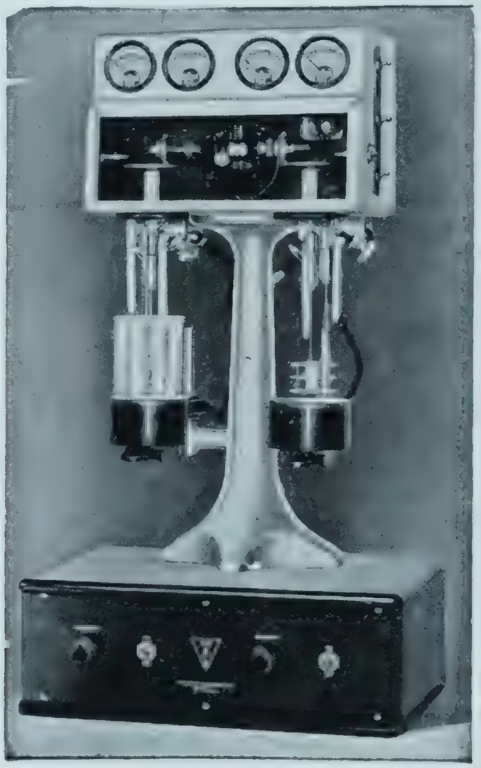

Fig. 80. Electrolytic apparatus with automatic washing equipment.
(Courtesy Wilkens-Anderson Co.)

f. Combination Method[66]

As an illustration of a method combining the information of the preceding methods, namely, dithizone extraction, electrolytic deposition of lead peroxide, and iodometric estimation, the following method is appended.

Prepare an acid solution of the lead specimen by one of the methods previously detailed. Add to an aliquot in a separatory funnel 20 ml. of citric acid solution, 20 g. of citric acid dissolved in water and make up to 100 ml., and 8 g. of sodium hexametaphosphate. Make this solution just alkaline with ammonium hydroxide, and add 10 ml. of potassium cyanide solution (10 g. of KCN dissolved in water and made up to 100 ml.). Extract with small portions of dithizone solution (50 mg. dithizone in 100 ml. of chloroform) until the color of one portion remains unchanged. Drain the successive chloroform extracts into a smaller separatory funnel containing 20 ml. of ammonium hydroxide (1:99), and shake as a means of washing the chloroform. When the extraction is complete, drain the combined portions of dithizone-chloroform solution, containing the lead, into a 150-ml. beaker and evaporate to dryness over a steam bath. After the chloroform has been completely evaporated, add 2 ml. of concentrated nitric acid, place a watch glass over the beaker, and boil until the gases evolved are colorless. Dilute to about 100 ml., heat to 75–80° C., add 2 ml. of potassium dichromate solution, and electrolyze, maintaining the stated temperature as directed in the preceding method. Dissolve the lead peroxide in a mixture of 2 ml. of potassium iodide (2 g. KI dissolved in water and made up to 100 ml.) and 4 ml. of acid sodium acetate solution (consisting of 20 ml. of saturated sodium acetate solution, 10 ml. of glacial acetic acid, and 70 ml. of water). Titrate with approximately 0.001 *N* sodium thiosulfate solution that has been previously standardized against a known amount of lead, as described in the foregoing. The very dilute thiosulfate solution may be protected from decomposition for several weeks by adding 1 per cent of amyl alcohol to the boiled water with which it is prepared.

g. Qualitative Test[67–69]

The microscopic test based on the identification of potassium copper lead hexanitrite is often used as a qualitative means of ascertaining if lead is present. The lead is precipitated as sulfide in the presence of ammonium sulfate and copper acetate, the copper acting as a collector. After careful washing of the filtered precipitate, the lead sulfide is dissolved in a few drops of concentrated nitric acid. A drop of this solution is evaporated to dryness on a microscope slide. Minute quantities of sodium acetate, acetic acid, and a small crystal of potassium nitrite are added. Lead, if present, crystallizes out as characteristic brown squares and cubes of potassium copper lead hexanitrite, $K_2CuPb(NO_2)_6$.

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[66] C. C. Cassil and C. M. Smith, *Am. J. Pub. Health, 26*, 902 (1936).

[67] R. U. Harwood and D. Brophy, *J. Ind. Hyg., 16*, 25 (1934).

[68] H. Behrens and P. D. C. Kley, *Mikrochemische Analyse,* Voss, Leipzig, 1915.

[69] A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases,* Service to Industry, Hartford, 1936.

4. Tetraethyl Lead

Tetraethyl lead is a colorless liquid with a specific gravity of 1.62 at 15° C. It boils at 200° C. with some decomposition and at 91° C. under 19 mm. of mercury pressure. It is insoluble in water. It is lipoid solvent and has some solvent action on rubber. The fact that it is a lipoid solvent makes it an industrial hazard not only because of inhalation but also by absorption through the skin. It decomposes when exposed to sunlight or evaporation and forms as one of its decomposition products triethyl lead, a poisonous compound.[70] The industrial hazard of tetraethyl lead is principally limited to its manufacture, to the preparation of "antiknock" mixtures, to the mixture of these with gasoline, and to the cleaning of tanks in which these materials have been stored.[71]

a. Determination

In order to trap any tetraethyl lead present as a true vapor or gas, one may use the following arrangement. Pass the air by suction, which may be supplied by a Hancock ejector, Hatch style, if compressed air is available, or by some other means through a tube $2^1/_2$ inches in diameter and 8 inches long tapering to the bottom to $^1/_2$ inch in diameter. The tube is filled with activated coconut-shell charcoal, supported in the tube by a fine-mesh copper screen. After sampling transfer the charcoal to a mason jar for transportation to the laboratory for analysis.[72]

Treat the charcoal with cold nitric acid for 24 hours. Filter and evaporate to dryness. Lead is estimated in the residue by one of the methods previously detailed.

The residue of charcoal is ashed and then lead is estimated in the ash. The results obtained by both determinations are added.[73]

b. Determination in Gasoline

Since tetraethyl lead is comparatively volatile, special precautions must be taken in order to estimate it in gasoline. Shake the sample of gasoline and transfer 25 ml. with the aid of a pipette to a Kjeldahl flask, containing 25 ml. of absolute ethyl alcohol. Add small portions of bromine, while shaking the flask vigorously, until a red color persists. Allow the mixture to stand overnight. Evaporate on a water bath to 10–15 ml. Add 25 ml. of concentrated nitric acid and evaporate to dryness on the water bath. Add an additional 25 ml. of concentrated nitric acid and 2 g. of potassium chlorate. Heat the mixture carefully and gently over a free flame in a hood. If all the organic material is not oxidized, repeat the nitric acid and perchlorate treatment.

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[70] F. B. Flinn, *J. Ind. Hyg., 8,* 51 (1926).

[71] W. Machle, *J. Am. Med. Assoc., 117,* 1965 (1941).

[72] C. P. Leake and J. J. Bloomfield in *U. S. Pub. Health Service, Bull. 163* (1926).

[73] Clark, Elvove, Remsburg, Hall, and Simkins in *U. S. Pub. Health Service, Bull. 163* (1926).

When all the organic material is oxidized, evaporate the mixture to dryness. Treat the residue with 50 ml. of water and 5 ml. of hydrochloric acid (1:1). Warm on a water bath until solution is complete. Transfer the solution from the Kjeldahl flask to a 500-ml. wide-mouth flask, and make up to a volume of about 200 ml. with the water washings from the Kjeldahl flask. Add a few drops of thymol blue, neutralize with 25 per cent sodium hydroxide solution free from iron and aluminum until a yellow color is obtained, and then make faintly pink with hydrochloric acid (1:1). From this point the Fairhill method or one of the other methods detailed for the estimation of lead may be followed.[74]

An alternative method[74] of preparation of a sample for the estimation of lead in gasoline is the following. Transfer 50 ml. of the sample to a dry 500-ml. wide-mouth flask. Add 10 ml. of a 30 per cent by volume solution of bromine in carbon tetrachloride, while keeping the flask in an ice bath to prevent overheating. Filter the precipitated solid through a prepared dry Gooch crucible and wash the flask and the Gooch crucible several times with anhydrous petroleum ether. Place the crucible in a 250-ml. beaker, add 10 ml. of concentrated nitric acid, and heat until no more bromine fumes are given off. Transfer the contents of the Gooch crucible to the beaker itself with the aid of a stirring rod. Remove the crucible, wash it well with water, and allow the washings to fall into the beaker. Bring the liquid to boiling and filter through another prepared Gooch crucible. Wash the crucible well with hot water, adding the washings to the main filtrate. From this point proceed as described with one of the methods for lead determination.

An alternative method depending on hydrolysis of the tetraethyl lead with hydrochloric acid, extraction of lead chloride with water, and subsequent estimation of lead is described by Calingaert and Gambrill.[75]

B. MERCURY

1. *Mercurialism*

Mercurialism is an illness that was known in ancient history, since quicksilver was used by goldsmiths. Mercury was one of the few metals well characterized by the alchemists and, indeed, was representative of metals as a class to them. With increase in the use of mercury in many industrial processes, such as the mercury boiler and catalytic applications, has also come the possible increase in the hazard of mercury poisoning.

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[74] *U. S. Pub. Health Service, Bull. 163* (1926).

[75] G. Calingaert and C. M. Gambrill, *Ind. Eng. Chem., Anal. Ed., 11*, 324, 445 (1939).

2. *Vapor Pressure of Mercury*

It is often not realized that mercury has a definite measurable vapor pressure at normal temperatures, which increases markedly with increase in temperature. This is illustrated by the following table:

TABLE 10

Vapor Pressure of Mercury[76]

Temperature, °C.	Vapor pressure, mm. of mercury	Theoretical concentration of mercury in the air	
		mg./liter	Ppm.
20	0.0013	0.0152	1.84
30	0.0029	0.0339	4.10
40	0.0060	0.0700	8.5
60	0.0300	0.3500	42.5
100	0.28	3.26	396.0
200	18.3	213.0	25,800.0
300	246.0	2879.0	348,000.0

3. *Industrial Exposure*

Because of its volatility there is considerable mercury vapor in the air wherever mercury is worked, as, for instance, in the manufacture of thermometers, barometers, mercury-vapor lamps, teeth fillings, pharmaceuticals (such as mercurial ointments), dyestuffs, and synthetic chemicals, among many other uses. There are mercury hazards in treating seeds with mercurial fungicides such as ethyl mercury phosphate and ethyl mercury chloride.[77]

Formerly one of the greatest sources of mercury poisoning in the manufacture of felt hats was in the "carrotting" of furs with "secret formulas" containing mercuric nitrate as a component. Fur cutters and felt-hat workers contracted mercury poisoning because this process contaminated the air in which they worked with mercury vapor and with mercury-bearing dust. The fine hairs of the fur of rabbits, hares, and other animals used in making felt are smooth and straight. By treating them with acid nitrate of mercury, they are made limp and twisted, which aids in the felting process. The use of secret formulas was begun about the middle of the seventeenth century in France and spread to other countries with the dispersion of the Huguenots. The process is termed carrotting because of the yellow color produced on the felt. The French formulas also include arsenic trioxide, white arsenic, and mercuric chloride.

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[76] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

[77] H. F. Schulte, *J. Ind. Hyg. Toxicol., 28,* 159 (1946).

Lloyd and Gardner[78] found by analysis that carrotted rabbit fur contained 0.09 to 0.17 per cent of mercury and that vapors escaping from the planker's acid vat contained 0.0012 per cent of mercury. A fringed cloth tied around the hood of the vat was found to contain 0.01 per cent of mercury. In this instance it is clear that mercury was deposited upon the cloth only by evaporation.

While the literature on mercurialism among fur-felt hatters contains many statements concerning the severity of the hazard among carrotters, it was shown by the study of the U. S. Public Health Service[79] that it is the workers who come in contact with the felt after carrotting that are in greater danger. This study also shows that the greatest part of the mercury hazard in this trade is in the form of mercury vapor rather than in the form of mercury-impregnated dust.

4. Toxicity and Physiological Response

The inhalation of relatively large concentrations of mercury vapor, as, for instance, in the case of a mercury-boiler leak,[80] is accompanied by the warning effect of a brassy taste in the mouth and discomfort in the throat. Longer exposure to amounts not capable of being tasted or smelled causes severe headache and, if exposure is continued, distress in the alimentary canal with either looseness or constipation.

Koelsch and Ilzhöfer[81] assert that from 0.4 to 1 mg. of mercury taken daily for a month will produce poisoning.

Turner[82] concluded that daily exposure to an atmosphere containing as little a quantity as 0.02 mg. of mercury per cubic foot of air, with a consequent absorption of from 0.771 to 1.2585 mg. daily, results in signs and symptoms of mercury poisoning in 2 to 3 months.

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[78] L. L. Lloyd and W. Gardner, *J. Soc. Chem. Ind., 31,* 1109 (1922).

[79] R. R. Sayers, P. A. Neal, R. R. Jones, J. J. Bloomfield, J. M. DallaValle, and T. I. Edwards, *U. S. Pub. Health Service, Bull. 234* (1937).

[80] *Chem. Met. Eng.,* "Process Industries—Flow Sheets and Data Book," p. 133.

[81] F. F. Koelsch and H. Ilzhöfer, *Zentr. Gewerbehyg.,* 7, 11, 17, 42 (1919); *J. Ind. Hyg., 2,* 135 (1920).

[82] J. A. Turner, *U. S. Pub. Health Repts., 39,* 329 (1924).

Nordlander[83] disputed this contention on the basis that Turner's analytical results were low and that therefore the amount of mercury inhaled actually must have been greater. He concluded that it requires greater amounts of inhaled mercury before poisoning takes effect.

Investigators of the U. S. Public Health Service[84] were inclined to agree with Nordlander. They found that from their data it was not possible at that time to define a reasonably safe maximum concentration of mercury in the work-room atmosphere. Symptoms of chronic mercurialism developed among individuals working in atmospheric concentrations ranging from 0.6 to 7.2 mg. of mercury per 10 cubic meters of air. The severity of chronic mercurialism and the percentage of persons affected increased with the degree of exposure to mercury. The incidence of chronic mercurialism increases rapidly with increasing mercury concentration after the concentration exceeds 2.0 mg. per 10 cubic meters.

One very interesting point observed by these investigators was that the small "back-shop" type of plants, even with their extremely insanitary conditions, had relatively small amounts of mercury vapor and dust in the air as compared with larger plants. They explained this by the fact that the small plants do not allow stock to accumulate but work intermittently as orders are received. For this reason, very little mercury is handled from day to day and practically no treated furs are allowed to accumulate in the factories. On the other hand, in the larger plants considerable quantities of mercury are being used and hundreds of thousands of treated skins and vast quantities of treated fur are continually present in the factory. These treated skins give off mercury vapor continually.

Other investigators insist that minute amounts are dangerous. Stock and Cucuel[85] believe that it is injurious to health to breathe continuously any air containing a few thousandths of a mg. of mercury per cubic meter of air, as did Turner. Goodman[86] proposed an approximate safe concentration of 0.25 mg. per cubic meter of air but agreed with a subsequent recommended toxic limit[87] of 0.1 mg. per cubic meter.

The question should certainly be resolved in the favor of those investigators who believe that lower limits of mercury are dangerous, for

[83] B. W. Nordlander, *Ind. Eng. Chem.*, *19*, 522 (1927).

[84] R. R. Sayers, P. A. Neal, R. R. Jones, J. J. Bloomfield, J. M. DallaValle, and T. I. Edwards, *U. S. Pub. Health Service, Bull. 234* (1937).

[85] A. Stock and F. Cucuel, *Ber.*, *67B*, 122 (1934).

[86] C. Goodman, *Rev. Sci. Inst.*, *9*, 233 (1938).

[87] M. Shepherd, S. Schukmann, R. H. Flinn, J. W. Hough, and P. A. Neal, *J. Res. Nat. Bur. Standards* (*Res. Paper 383*), *26*, 357 (1941).

keeping the amount of mercury down to those limits unquestionably will diminish the possibility of mercury poisoning.

5. *Sampling of Mercury*

Mercury vapor in the air may be detected directly by means of the General Electric selenium sulfide detector or by photoelectric detectors. Mercury-bearing dust may be sampled by the use of impinger devices. However, mercury-bearing fur dust is also fat bearing and consequently difficult to wet and retain in an impinger. In such instances it is better to use 25 per cent ethyl alcohol-water mixtures as the collecting medium. Nordlander[88] points out that where aqua regia is used as the absorbent for mercury vapor, errors may be introduced because a white coat of mercuric chloride forms around a drop of mercury, protecting it from further solution. Even nitric acid alone as the absorbent is better.

One of the best means of trapping mercury vapor is the use of traps immersed in freezing mixtures such as liquid air, liquid nitrogen, or a mixture of solid carbon dioxide and ether.[89–91]

6. *Detection and Determination of Mercury*

a. Selenium Sulfide Detector[92,93]

This method is based on the reaction between active selenium sulfide and mercury vapor. The selenium sulfide is applied as a coating to paper and the coated paper is blackened on exposure to air containing mercury vapor, the degree of blackening being a function of time of exposure, concentration of mercury vapor, and other factors, which can be definitely controlled. At a velocity of 1 meter per second of the impinging air and at a reaction temperature of 70° C., a concentration of mercury in the air as low as 1 in 4 million parts by volume can easily be detected after 4 minutes' exposure.

Preparation of Active Selenium Sulfide. Saturate a solution of aluminum chloride, containing about 100 mg. of aluminum per liter, with hydrogen sulfide at room temperature, preferably in a flask that is partly closed in order to retain an atmosphere of hydrogen sulfide above the liquid and thus promote its absorption by the solution during the reaction. Vigorous stirring is also useful for the same purpose. While continuing the current of hydrogen sulfide, add normal selenious acid solution slowly, delivering it below the surface of the reaction mixture in the flask. A yellow precipitate separates out readily. A moderate temporary excess of the acid will form a sol which quickly clears up if the addition is stopped for the time, but too much will give trouble. The operation should be carefully watched to keep the hydrogen sulfide in excess.

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[88] B. W. Nordlander, *Ind. Eng. Chem.*, 19, 522 (1927).
[89] A. Stock and R. Heller, *Z. angew. Chem.*, *39*, 466 (1926).
[90] A. Stock and F. Cucuel ,*Ber.*, *67B*, 122 (1934).
[91] A. M. Fraser, *J. Ind. Hyg.*, *16*, 67 (1934).
[92] B. W. Nordlander, *Ind. Eng. Chem.*, *19*, 518 (1927).
[93] L. R. Biggs, *J. Ind. Hyg. Toxicol.*, *20*, 161 (1938).

Filter, wash, and dry the precipitate. It is a fine yellow powder, and can be dried on the steam bath without turning red. Short exposure to strong sunlight causes it to turn slightly reddish, but it goes back to yellow in darkness. Long exposure gives a permanent red to reddish violet. On rubbing it becomes strongly electrified and it is probable that this electrification has some connection with the tenacity with which it adheres to paper. When kept in the dark no decrease in sensitivity to mercury vapor with age has been detected.

The selenium sulfide is applied to paper by dipping a pad of cotton wool into the powder and rubbing lightly over the surface of the paper until a uniform film, judging by the color, is formed. The operation is easy if conditions are right. Among the most important of these conditions is the character of the paper. It should be smooth and dense, but not so highly glazed that adhesion and distribution of the powder are poor. The paper used by Nordlander is "Warren's Cumberland Coated Paper, 70 lbs." A successful result is characterized by a surface of even light yellow and of a durability approaching that of a dyed surface. The powder can also be applied to other carriers, such as wood, finely ground or etched glass, celluloid, and certain metals like lead, to produce a surface sensitive to mercury vapor.

Procedure. A portable apparatus has been developed by the General Electric Co The air or gas to be analyzed is blown into the apparatus by means of a small blower, the velocity of the air current being measured through a tap by a pressure gauge, which serves as a flowmeter. By turning an opening ring, the incoming air current may be bled off, making possible an adjustment of velocity. The air then passes over an electric heater to attain the proper temperature and into another tube, which ends in a nozzle. The selenium sulfide sensitized paper is exposed to the air containing the mercury vapor opposite the nozzle. After impinging against the paper, the air is turned back into the annular space between the nozzle and the housing of the apparatus and is discharged through holes. In this space the outgoing air passes over an adjustable thermoregulator, which controls the heating current around the incoming air.

The relation of time of exposure to the degree of blackening furnishes a very simple way of making a color scale from which, by comparison with the results from a test with a gas of unknown mercury vapor content, almost any concentration can be estimated. A series of prints is made up at an arbitrarily chosen concentration by varying the times of exposure. One can thus get the densities of the prints to increase in any convenient way, preferably in arithmetical progression. This series is naturally limited to the densities that can readily be differentiated by the eye, but the range of concentrations can be indefinitely extended simply by changing the time of exposure. It is evident that by then applying the above relation, the scale so produced can be calibrated and used to determine any concentration of mercury vapor. In case of low mercury concentrations it is necessary to increase the time of exposure, but with high mercury concentrations the reverse procedure should be adopted. In this way a scale has been made up which can, by changing the time of exposure in geometrical progression from 8 minutes to 1 minute, be used to measure any concentration between 1:8,000,000 and around 1:15,000, the latter corresponding to the saturation of air with mercury at the standard reaction temperature of 70° C.

b. Photoelectric Detector[94]

Another mercury detector depends on the scattering of the resonance radiation of mercury (ultraviolet light with a wave length of 2537 Å. units) by mercury vapor. The degree of opaqueness to light of this wave length of the air tested is a measure of the concentration of mercury vapor in the air. The estimation is made photoelectrically and gives a rapid reading of the mercury-vapor concentration in the air, even to as low a concentration as 1 part of vapor per billion parts of air. Still another type of photoelectric detector, the R & H Tri-Per Analyzer, is briefly described in Chapter XII.

c. Electrolytic Method

Mercury vapor can be estimated conveniently by the selenium sulfide detector but this detector is inapplicable for the estimation of mercury compounds or mercury-bearing dust. The electrolytic method as modified by Stock and Cucuel[95] and by Fraser[96] can be used for all types of air samples contaminated by mercury. In principle the contaminated air is trapped by passing it through a tube chilled by liquid air, liquid nitrogen, or a mixture of solid carbon dioxide and ether. The deposited mercury is then dissolved in chlorine water and may subsequently be estimated by one of two methods, namely, electrolytic deposition alone or a combination of electrolytic deposition and micrometric measurement. Micrometric estimation consists of isolating the mercury as the metal and measuring the diameter of the drop produced by means of a microscope.

Mercury-bearing dust may be sampled with a Greenburg-Smith impinger. However, since most of this type of dust is also oil bearing, the dust is trapped in water and alcohol. Then the organic material must be destroyed.[97]

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[94] W. J. Burke, S. Moskowitz, and B. H. Dolin, *N. Y. State Ind. Bull. 18*, 235 (1939).
[95] A. Stock and F. Cucuel, *Ber., 67B*, 122 (1934).
[96] A. M. Fraser, *J. Ind. Hyg., 16*, 67 (1934).

Transfer the sample to a 500-ml. Kjeldahl flask and boil off the alcohol very rapidly for 5 to 10 minutes. Cool, add 10 ml. of concentrated sulfuric acid and then 4 g. of potassium permanganate. Wash down the neck of the flask with water. Allow the sample to digest at a temperature just below boiling for 2 hours. Decolorize with oxalic acid, for which 3 g. is generally required, warming if necessary. If the reaction mixture is not cold, add the oxalic acid in small amounts during this step. Transfer the solution to a 250-ml. wide-mouth glass-stoppered centrifuge bottle, add 1 ml. of 0.5 per cent copper sulfate solution, and then pass in hydrogen sulfide for about $^1/_2$ hour. Stopper the flask and permit the precipitate to settle overnight. Wash by centrifuging. Pass chlorine gas into the centrifuge bottle containing the washed mercury and copper sulfides after the addition of 5 ml. of water. Solution is generally effected in 15 minutes. Aspirate air through the flask to remove the excess chlorine.

Transfer this solution to a 50-ml. beaker. Add 2 ml. of a saturated solution of oxalic acid and 5 ml. of a saturated ammonium oxalate solution. Plate out the mercury, using a pure gold cathode, 1 by 3 cm. and $^1/_4$ mm. thick. Keep the voltage at about 1.3–1.5 volts. At this voltage, 18 to 24 hours is required for complete deposition. The gold electrode can be easily made in the laboratory. Cut a piece of gold foil to the specified dimensions and weld it to a platinum wire by heating the wire and foil in position on an anvil with a Bunsen flame, finally tapping gently with a small hammer. Care must be taken not to melt the gold by excessive heating. Wash the electrode upon which both copper and mercury have deposited with water, alcohol, and ether, successively, dry in a desiccator, and weigh on a micro balance.

After weighing, place the electrode in a Pyrex combustion tube, pass through a stream of hydrogen, heat the tube carefully, and drive off the mercury. Cool in a desiccator and weigh again on a micro balance. The difference in weight represents mercury. Never dry the original mercury deposit in an oven.

If the original sample consists of mercury vapor trapped in a U-tube immersed in a freezing mixture and no organic matter is present, the analysis may be begun from the point of passing in the chlorine gas in order to dissolve the mercury. In other words, the acid digestion and copper coprecipitation of sulfide may be eliminated.

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[97] F. H. Goldman, *U. S. Pub. Health Service, Reprint 1804* (1937).

d. Dithizone Method

Dithizone, diphenylthiocarbazone, may also be used for the estimation of mercury.[98,99] This method is based on the following principles. When a dilute acid solution containing mercury and other metals is shaken with a chloroform or carbon tetrachloride solution of dithizone, the normal green color of dithizone solution changes to a bright orange yellow color attributable to the formation of a soluble organic mercury complex, which approaches two molecules of dithizone to one atom of mercury. (One mg. of mercury reacts with 2.6 mg. of dithizone.) The yellow color persists as long as the mercury is in excess. When sufficient dithizone is added to react with all the mercury present, any excess of the reagent turns the solution green or red or reddish violet, depending upon whether traces of copper are present in the mixture. The fact that mercury under proper conditions will react with dithizone first is the basis of a determination of mercury by titration. High concentrations of copper must be removed before the titration of the mercury. This may be done by the addition of potassium iodide, for in the presence of iodide the copper is extracted with dithizone, whereas mercury remains in the aqueous solution. Mercury cannot be extracted or titrated with dithizone in acid solution when iodides are present but it can be extracted in ammoniacal solution. It can also be extracted from an acid solution containing iodides by the use of sodium diethyldithiocarbamate and chloroform as the extractant.

Procedure.[100] Collect and trap the mercury-bearing dust by means of a Greenburg-Smith impinger device or by some other adequate dust collector. If an impinger is employed, use water as the collecting medium, or if the dust is oil or fat bearing, use water and alcohol.

Digest the sample of collected dust and the washings under a reflux condenser with about 25 ml. of concentrated nitric acid, 2 ml. of concentrated sulfuric acid, and sufficient potassium permanganate until the organic matter is completely destroyed. Add more permanganate and nitric acid if necessary. Remove the excess permanganate and the manganese dioxide by the dropwise addition of 30 per cent hydrogen peroxide. Expel the dissolved oxygen by boiling. Cool, add about 0.5 g. of hydroxylamine hydrochloride, and extract the solution by shaking with successive portions of a chloroform solution of dithizone, containing 25

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[98] H. Fischer, *Z. angew. Chem., 42,* 1025 (1929).

[99] W. O. Winkler, *J. Assoc. Official Agr. Chem., 18,* 638 (1935).

[100] W. J. Burke, S. Moskowitz, and B. H. Dolin, *N. Y. State Ind. Bull. 18,* 235 (1939).

mg. per liter, until it is present in excess, that is, the green color of the dithizone predominates over the yellow of the mercury complex.

Treat the chloroform extract with 50 ml. of water at 50–60° C., 2 ml. of 5 per cent potassium permanganate solution, and 2 ml. of sulfuric acid (1:1). The mercury passes into the aqueous layer. Withdraw the chloroform layer and discard. To the aqueous solution, add sufficient 10 per cent sodium or potassium nitrite solution to react with the excess permanganate. Destroy the free nitrous acid left by the addition of about 0.5 g. of hydroxylamine hydrochloride and heat just to boiling.

If large amounts of copper are present, the mercury may be inactivated by the addition of iodide ion. On re-extracting with dithizone, the copper is removed and the mercury is left in the aqueous solution. After the excess iodide is destroyed or the solution made ammoniacal, the mercury may be estimated by the titration procedure described below. Small amounts of copper will not interfere with the analysis for mercury, since only a small percentage of the copper present will be extracted with dithizone from a solution at a pH 2, which is sufficiently acid to permit complete extraction of the mercury present.[101]

Titrate the cool solution in a separatory funnel with a carbon tetrachloride solution of dithizone containing about 1.25 mg. dithizone per liter. Add small portions of this solution until it is present in excess. Use standard mercuric nitrate solution, containing exactly 10 mg. of mercury per liter, for back-titration of the excess. Determine the exact strength of the dithizone solution each time it is used by treating a solution containing 0.1 mg. of mercury as mercuric nitrate in the same manner as described for a test sample. All the reagents used must be as pure as it is possible to procure them, and blank determinations on water alone must be performed to determine the mercury content of the water and the reagents used in the analytical procedure. Subtract the mercury found in the blank from that found in the test sample to ascertain the quantity actually present in the material analyzed.

e. Polejaeff Method

In the Polejaeff[102] methods, the mercury in the air is absorbed in a solution of iodine in potassium iodide in absorbers. The unknown is added to a mixture of copper sulfate and sodium sulfite in colorimeter tubes. The color produced is compared with that produced by standards made with mercuric chloride. Barnes[103] modified these methods by standardizing the method of sampling, the reagents, and the order of the addition of the reagents.

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[101] H. J. Wichmann, *Ind. Eng. Chem., Anal. Ed.*, *11*, 66 (1939).

[102] A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases*, Service to Industry, Hartford, 1936.

[103] E. C. Barnes, *J. Ind. Hyg. Toxicol.*, *28*, 257 (1946).

Sampling. Trap mercury vapor, dust, and mercury-bearing compounds by drawing air at the rate of 1 c. f. m. through a standard impinger containing a 0.25 per cent solution of iodine in a 3 per cent aqueous solution of potassium iodide. Prepare the sampling solution as directed below. Place the volume required for sampling, usually from 50 to 100 ml., in 150-ml. wide-mouth, glass-stoppered bottles. Transfer the sampling solution to the impinger at the sampling point. Return the sampling solution to the 150-ml. flask after sampling and rinse the impinger flask with 20 to 50 ml. of sampling solution.

Reagents. Sampling Solution. Dissolve 30 g. of potassium iodide in 30 ml. of water. Dissolve 2.5 g. of iodine in this concentrated potassium iodide solution. Transfer to a 1-liter volumetric flask, wash the beaker in which the iodine was dissolved thoroughly with water, add the washings to the flask, and make to volume.

Standard Mercury Solution. Dissolve 0.135 g. of mercuric chloride, $HgCl_2$, in 1 liter of sampling solution. This solution contains 0.1 mg. of mercury per ml. Dilute this stock standard mercury solution to 10 micrograms of mercury per ml. with additional sampling solution. The optimum range of standards lies between 3 and 20 micrograms but the range from 1 to 100 micrograms can be covered. Barnes suggests microgram standards of 3, 3.5, 4, 4.5, 5, 5.5, 6, 7, 8, 9, 10, 11, 12, 14, 16, 18, and 20 where greater accuracy is desired, and standards of 3, 4, 5, 6, 8, 10, 15, and 20 micrograms of mercury for less exacting comparison. Draw the required amount of the 10-microgram standard solution from a micro burette into a 50-ml. Nessler tube, complete the volume to 5 ml., and proceed with the method as detailed.

Procedure. Determine the total volume of the sample. Make a preliminary test as described below to ascertain the range of mercury concentration. Dilute the sample or an aliquot of the sample to a known volume with additional sampling solution to place the mercury concentration within the optimum range.

Transfer a 5-ml. aliquot of the sample or diluted sample to a 50-ml. Nessler tube. Add 1 ml. of copper sulfate solution (10 g. $CuSO_4.5H_2O$ dissolved in water and made to 100 ml.) and swirl. Add 2 ml. of 3 N sodium sulfite solution (75.65 g. of $Na_2SO_3.7H_2O$ dissolved in water and made to 200 ml.) and swirl or shake, continuing this action for 0.5 minute. Permit the precipitate to settle. This is white if mercury is absent and pink orange if mercury is present. Treat the standards in a similar way. Shake the unknown and the standards at the same time to resuspend the precipitates and compare them.

Calculation. Calculate the concentration of mercury in the air by use of the following formula:

$$C = \frac{A \times B \times D}{E \times 141.6}$$

where:

A = micrograms of mercury found in the 5-ml. aliquot used for analysis
B = volume of impinger sampling solution, including the washings
D = factor by which impinger sampling solution and washings were diluted. (Thus if 50 ml. were diluted to 250 ml. the factor would be 5.)
E = cubic feet of air drawn through the impinger. (At the standard flow rate of

1 c. f. m., E would equal the time in minutes used for the collection of the sample.)

C = average concentration of mercury in air where the impinger sample was taken, expressed in mg. per cubic meter

The factor 141.6 is used to convert the result from micrograms to milligrams, from cubic feet to cubic meters, and to account for the 5-ml. aliquot.

Mercuric oxide, mercuric nitrate, mercurous nitrate, mercuric chloride, mercuric iodide, and mercuric acetate are soluble to the extent of 0.2 g. or more in 100 ml. of iodine-potassium iodide sampling solution. Phenyl mercuric phthalate (0.04 g. per 100 ml.) and phenyl mercuric salicylate are slowly soluble. Metallic mercury is also slowly soluble.

f. Sulfide Method

Minot[104] used the sulfide method to estimate the quantity of mercury present in hatters' felt. The felt is first oxidized by the use of nitric acid and potassium permanganate. It is then precipitated as the sulfide. The sulfide is purified by solution in sodium hydroxide and after reprecipitation as the sulfide it is estimated gravimetrically.

Treat 10 g. of the fur with 100 ml. of concentrated nitric acid. Allow to stand overnight. In the morning add 100 ml. of water, boil gently, and add small amounts of potassium permanganate. Continue the addition of permanganate until all organic matter is destroyed, which is shown by an excess of undissolved manganese dioxide precipitate or by a permanganate color after the solution has been boiled several minutes. Reduce the excess permanganate by boiling the solution with 0.5 g. of oxalic acid. The solution should now be clear and light straw-colored. Almost neutralize by the addition of sodium carbonate in small amounts. With the solution still acid, precipitate the mercury with hydrogen sulfide. Precipitation in nitric acid solution separates mercury from the other heavy metals. The mixture is filtered. Wash the precipitate with hot water and dissolve in aqua regia. Repeatedly wash the filter paper with boiling water. Filter, neutralize the filtrate with sodium hydroxide, and precipitate the mercury with ammonium sulfide. Add sodium hydroxide until the solution appears lighter colored. Then add still more sodium hydroxide while boiling until the mixture forms a clear solution. The mercuric sulfide is thus converted to the soluble sodium sulfo compound, $Hg(SNa)_2$. From this solution, mercury is reprecipitated as sulfide in a filtrable form by excess solid ammonium nitrate. Boil with sodium sulfide to remove excess ammonia and to convert any sulfur present to sodium thiosulfate. Allow to stand overnight and filter on a tared Gooch crucible. Dry at 110–120° C., cool in a desiccator, and weigh. The weight is taken as mercuric sulfide, from which the weight of mercury is obtained by multiplication by the proper factor.

The following reactions take place in the method.

$$HgS + 2NaOH + (NH_4)_2S \rightarrow Hg(SNa)_2 + 2NH_4OH$$
$$Hg(SNa)_2 + 2NH_4NO_3 \rightarrow 2NaNO_3 + (NH_4)_2S + HgS$$

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[104] A. S. Minot, *J. Ind. Hyg.*, *4*, 253 (1922–23).

g. Other Methods

Other methods for the determination of mercury are those of Pyankoff[105] and Moldavsky,[106] which are based on the formation of mercuric iodide and mercuric bromide.

In the Pyankoff[105] method, air is aspirated through a U-tube containing crystals of iodine in the curve. After sampling is completed, the tube is immersed in a water bath at about 70° C. to warm and air is drawn through to remove the excess iodine. The mercuric iodide crystals which remain in the tube are dissolved in alcohol, the heating aids the solution of yellow mercurous iodide, if formed, and the solutions are transferred to Nessler tubes or other colorimetric tubes. A series of standards is prepared within the range expected and to each tube is added 0.5 ml. of hydrogen sulfide water. The brown colors developed are compared. Alternatively, the mercury salts may be dissolved in ether, transferred to a tared dish, dried, and weighed.

In the Moldavsky[106,107] method, the mercury in the air is absorbed by the use of gaseous bromine. The mercuric bromide solution is transferred to a beaker, chlorine water is added, and the solution is evaporated in a vacuum desiccator over sodium hydroxide. A drop each of sodium acetate and of alcoholic diphenylcarbazone solution is added. The color thus produced is compared with a series of standards.

Radioactive mercury has been applied as a tracer for the measurement of mercury vapor in air.[108] Using radioactive mercury of atomic weight 197 with a half period of 25 hours, an average concentration of 0.01 mg. of mercury per cubic meter of air was found to be present in a particular industrial operation suspected of causing chronic mercurialism. This technique is said to be capable of detecting 10^{-8} g. of mercury.

C. ARSENIC

1. *Arsenic Poisoning*

Mention poison to a layman and likely as not he will think of arsenic. With growth in the use of arsenic as a benefactor of mankind—note, for example, its use in arsenicals and in fungicides and insecticides—have also come the dangers associated with arsenic as a poison. Our present-day civilization almost cannot continue without the use of these materials, but we must eat and we must therefore attempt to keep the presence of arsenic at a minimum. The hazards associated with the use of arsenic in industry are many. One particular hazard, in reality not attributable to the use of arsenic compounds as such, but rather because the arsenic is present as a contaminant, is the danger of the formation of arsine (arseniureted hydrogen) whenever hydrogen is being evolved in any step of an industrial process. Another danger is the possible hazard from arsenic-contaminated organic chemicals manufactured from arsenic-contaminated sulfuric or nitric acids, which are often used in making organic chemicals. Smelting of arsenical ores, manufacture of paints, dyes, insecticides, fungicides, drugs, and felt hats, and curing hides are among the varied industries in which arsenic is a hazard. An extremely dangerous arsenic chemical is arsenious chloride (arsenic trichloride), which can cause death through inhalation or even by direct application to the skin.[109]

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[105] V. A. Pyankoff, *J. Applied Chem. U.S.S.R., 9,* 580 (1936); *Chem. Abstracts, 30,* 7488 (1936).

[106] A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases,* Service to Industry, Hartford, 1936.

[107] L. R. Moldavsky, *Zhur. Prikladnoi Khim., 3,* 955 (1930); *Chem. Abstracts, 25,* 1179 (1931).

[108] C. Goodman, J. W. Irvine, and C. F. Horan, *J. Ind. Hyg. Toxicol., 25,* 275 (1943).

2. Actual Role of Arsenic as Industrial Hazard

One of the difficulties associated with industrial poisoning resulting from arsenic is the actual role that the industrial hazard plays. Cannon[110] says that the effects of arsenic as observed in the majority of cases of chronic arsenic poisoning are not due to the arsenic derived from any single source, but from the combined effects of arsenic taken in from a multiplicity of sources, and in a great variety of forms. It is virtually impossible under present living conditions to remove a person from all contacts with arsenic.

One of the great sources or arsenic intake is the arsenic present in foods. Some of this is so-called natural arsenic, that is, the arsenic that is found in marine food products such as fish or lobster. Arsenic in foods is also due to the addition of insecticides and fungicides to fruits and vegetables. In order to keep the possibility of poisoning from this source to a minimum, there is a U. S. Government tolerance of 0.01 grain per pound, or 1.4 parts per million, of arsenic in foodstuffs. This has been increased to 0.025 grain per pound (3.58 parts per million) for spray residue.[111]

The maximum allowable concentration suggested by the American Standards Association as an American War Standard[112] was 1.5 mg. of arsenic, calculated as arsenic, per 10 cubic meters of air. Governmental hygienists[113] suggest 0.5 mg. per cubic meter. Higher concentrations are recommended by others.[114,115]

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[109] S. Delépine, *J. Ind. Hyg.*, *4*, 346 (1922–23).

[110] A. B. Cannon, *N. Y. State J. Med.*, *36*, 219 (1936).

[111] Federal Security Agency, Social Security Board, Washington, D. C., August 10, 1940.

[112] *Am. Standards*, Z37.9–1943.

The aforementioned discussion holds true for arsenic compounds but not for gaseous arsenic compounds. The type of poisoning caused by arsine is entirely typical for it is one of the very few hemolytic poisons encountered in industry.[116]

Because of its historic position as a poison, arsenic was one of the first elements for which methods to detect minute quantities were developed. One need but mention the names of Berzelius and Marsh to recall the qualitative and quantitative arsenic mirror tests developed.

3. Sampling of Arsenic

Arsenic compounds fall into three main groups, solid or liquid inorganic arsenic compounds, solid or liquid organic arsenic compounds, and volatile compounds of both groups. Arsenic-bearing dust and spray of the first two groups may be trapped by means of impinging devices, filtering devices, or bubblers containing absorbing agents such as sodium hydroxide, and bromine in potassium bromide or bromine water. The electrostatic precipitator is recommended for the sampling of arsenical fumes. Volatile arsenic compounds should be trapped by adsorption on silica gel or by absorption in silver nitrate solution or some volatile solvents in bubblers. The vapors of volatile arsines can be recovered[117] by distillation from the silica gel into an oxidizing mixture of sodium peroxide and sodium carbonate. Care must be taken whenever the possibility of forming arsenious chloride exists that an oxidizing medium is present so that no arsenic may be lost.

4. Acid Digestion

Because arsenic-bearing compounds are often organic compounds, some description of the customary methods for the destruction of organic matter is appropriate at this point. There are two general methods for the destruction of interfering organic matter. The first is called the "wet-ash," or acid-digestion, method and the second is ordinary ashing by means of heat with or without the aid of an "ash-aid" mixture or of an alkaline fixative for volatile metals, such as arsenic, antimony, mercury, or tin. Acid digestion is to be preferred for these metals except in the instance of antimony.

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[113] Threshold limit value adopted at meeting of American Conference of Governmental Industrial Hygienists, April, 1948.

[114] W. A. Cook, *Ind. Med., 14,* 936 (1945).

[115] R. M. Watrous and M. B. McCaughey, *Ind. Med., 14,* 639 (1945).

[116] I. Guelman, *J. Ind. Hyg., 7,* 6 (1925).

[117] M. Jurecek, *Collection Czechoslov. Chem. Communications, 6,* 468 (1934); *Chem. Abstracts, 29,* 705 (1935).

Transfer the sample or an appropriate aliquot or portion containing the arsenic to an 800-ml. Pyrex Kjeldahl flask. If the sample is a liquid and an oxidizing medium is present so that no arsenic will be lost on evaporation, the sample may be concentrated by evaporation. Add 50 ml. of concentrated nitric acid and then carefully add 20 ml. of concentrated sulfuric acid. Heat cautiously so that no excessive foaming takes place. Add nitric acid in small portions until all the organic matter is destroyed. This point is reached when no further darkening of the solution occurs on continued heating after the production of a clear solution and copious fumes of sulfur trioxide. Cool. Add 75 ml. of water and 25 ml. of a saturated solution of ammonium oxalate to aid in the expulsion of nitrogen fumes. Evaporate again until the appearance of sulfur trioxide fumes. Cool, dilute with water, transfer to a 500-ml. or 1-liter volumetric flask, and make to volume. Use aliquot portions for analysis as needed.

Wet ashing by means of nitric acid and potassium permanganate and by means of sulfuric acid and potassium permanganate has been described in connection with the methods for the estimation of mercury. In recent years methods of ashing by means of nitric and perchloric acids[118–120] have been developed in order to overcome the difficulties presented by volatile substances or those having an appreciable vapor pressure at the boiling temperature of a mixture of nitric and sulfuric acids, or which produce an insoluble precipitate in those acids. The author finds it difficult to recommend these procedures, for ashing with perchloric acid is extremely dangerous and serious explosions have occurred during its use. All the details may be found in the literature.

5. *Detection and Determination of Arsenic*

a. Reinsch Test

The Reinsch test is a simple though not very sensitive one. It is based on the deposition of arsenic from solution as a copper arsenide. The test may very often be applied directly without previous destruction of

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[118] J. E. Gieseking, S. H. Snider, and C. Getz, *Ind. Eng. Chem., Anal. Ed.*, 7, 185 (1935).

[119] H. W. Gerritz, *Ind. Eng. Chem., Anal. Ed.*, 7, 167 (1935).

[120] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products*, Van Nostrand, New York, 1945.

organic matter. Place 200 ml. of the suspected arsenic-bearing material, if trapped in water by an impinger or a bubbler device, in a casserole, and acidify with 1 ml. of arsenic-free hydrochloric acid. Evaporate to one-half its volume. Add 15 ml. more of hydrochloric acid and also a piece of pure burnished copper foil. Keep the liquid simmering for an hour and replenish the water lost by evaporation from time to time. If at the end of this time the copper foil remains bright, arsenic is not present in greater quantity than traces. If the copper has a black or brown deposit, remove it and wash well with water, alcohol, and ether, and dry. Place the foil in a subliming tube and heat over a low flame. If a sublimate is present, examine it under a microscope. Arsenic forms tetrahedral crystals in contradistinction to mercury, which forms globules. Antimony, silver, and bismuth will also give a deposit on the copper foil but will not sublime with the application of heat.

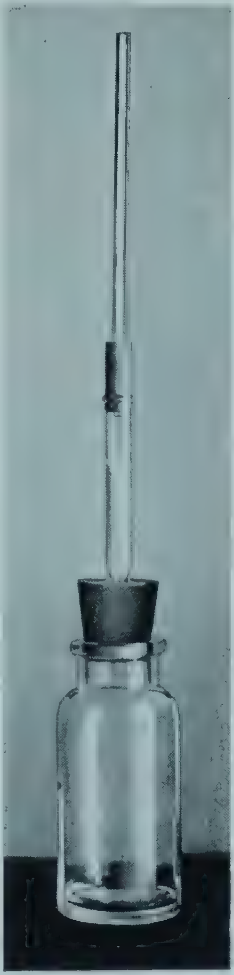

Fig. 81. Gutzeit generator.

b. Gutzeit Method[121]

The Gutzeit method is based on the liberation of arsine under carefully controlled conditions from an arsenic solution. The arsine subsequently reduces mercuric bromide on a prepared strip of paper with the production of stains. The stain, if the method is followed in detail, is proportional to the amount of arsenic present.

Prepare a generator (Fig. 81) as follows: Use a 2-ounce, wide-mouth bottle. Equip the bottle by means of a perforated stopper with a glass tube 1 cm. in diameter and 6–7 cm. long, with an additional constricted end to facilitate connection. Place a small wad of glass wool in the constricted bottom end of the tube and add 3.5 to 4 g. of 30-mesh clean sand. Moisten the sand with 10 per cent lead acetate solution and remove the excess by light suction. The lead acetate is used to remove any hydrogen sulfide that might be generated along with the arsine and thus vitiate results, if permitted to reduce the mercuric bromide. Connect the tube by means of a rubber stopper with a narrow glass tube 2.6–2.7 mm.

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[121] *Methods Assoc. Official Agr. Chemists,* 6th ed., 1945.

in internal diameter and 10–12 cm. long, and place in this tube a strip of mercuric bromide paper. These strips may be made by cutting paper similar to Whatman No. 40 filter paper into strips exactly 2.5 mm. wide and about 12 cm. long. Commercial strips are available. Soak the strips for 1 hour or longer in a fresh 3–6 per cent solution of mercuric bromide in 95 per cent alcohol. Dry and use within 2 days. For approximately quantitative work, these strips may be stored in a well-stoppered blackened tube.

Instead of preparing strips each time a determination is to be made, Goldstone[122] suggests that a sheet of 32 strips be cut into 9-cm. lengths, which may be suspended permanently in the alcoholic mercuric bromide solution stored in a 10-ml. glass-stoppered cylinder. Withdraw the strips as required, press immediately between filter paper, and permit the strips to dry in air for 0.5 hour before use.

Determine the acid in an aliquot of the solution prepared from the wet ash as described above. Place aliquots, not to exceed 30 ml., depending on the amount of arsenic trioxide, 0.01 to 0.03 mg., in the Gutzeit generator. If the aliquot contains only hydrochloric acid, add sufficient hydrochloric acid to make a total volume of 5 ml. If it contains sulfuric acid, add sufficient arsenic-free 25 per cent sodium hydroxide to exactly neutralize it and add 5 ml. of hydrochloric acid; or add sufficient hydrochloric acid to the sulfuric acid in the aliquot to make a total volume of 5 ml. Cool, if necessary, and add 5 ml. of potassium iodide solution (15 g. of potassium iodide dissolved in water and made up to 100 ml.) and 4 drops of stannous chloride solution (40 g. of arsenic-free stannous chloride, $SnCl_2.2H_2O$, in hydrochloric acid made up to 100 ml. with hydrochloric acid). Add a piece of activated zinc (prepared by placing the zinc in contact with hydrochloric acid (1:3), to which has been added 2 ml. of the stannous chloride reagent and allowing the action to proceed for 15 minutes) 10 to 15 g. in weight or 2 to 5 g. of granulated zinc, center the strip of mercuric bromide paper in its tube, and set the tubes in position.

Immerse the apparatus in a water bath kept at 20–25° C. to within 1 inch of the top of the narrow tube and allow the evolution of the arsine to proceed for 1 hour or 1$^1/_2$ hours. Remove the strip and average the length of the stains on both sides in mm. Locate the length of the unknown on a standard graph and read off on the abscissa the quantity of arsenic present. The graph may be made by running known quantities of arsenic by the above method, using length of stain as ordinates and mg. of arsenic trioxide as abscissas. Many authorities advise against the use of a standard graph on the ground that one cannot be prepared. They advise the running of a series of controls with every unknown determination.

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[122] N. I. Goldstone, *Ind. Eng. Chem., Anal. Ed., 18,* 797 (1946).

All the reagents used in this determination should be arsenic free. However, as a precaution, it is best to run blanks on the reagents. In some cases the test may be made without previous destruction of organic material but the results obtained are probably only approximate. An aliquot containing 0.02 to 0.025 mg. of arsenic trioxide is considered optimum for reading the stain.

Clarke[123] says that general experience has made it plain that not one of the various modifications of the Gutzeit method can be used by the average analyst with the assurance or even probability that his results will be accurate unless he attains considerable experience in its use.

Goldstone Modification. The Gutzeit method for arsenic is an empirical one. It requires strict adherence to all details. To overcome one source of error, namely, the uneven evolution of hydrogen, Goldstone[124] suggested the use of short zinc rods treated so that a constant surface area would be exposed and thus a relatively even evolution of hydrogen would result.

Preparation of Zinc Rods. Clamp a 15- by 125-mm. Pyrex test tube on a stand in a vertical position, place a 6-inch stick of arsenic-free zinc into the tube, and heat carefully with a Bunsen burner until the zinc melts and fills the entire tube. As an alternative procedure, melt the zinc in a beaker and pour the molten metal into a preheated Pyrex tube. Tap the tube to dislodge any air pockets that may have formed and allow the mass to solidify gradually, playing the flame on the upper portion in order to make this section solidify last. This precaution prevents the formation of a hollow core attributable to the contraction of the metal as it solidifies and insures a solid, uniform cylinder of zinc metal. Allow to cool and remove the cylinder by breaking the test tube. Cut the cylinder into lengths slightly less than the diameter of the generating bottle with the aid of a hack saw, grind the ends smooth with an emery wheel, and coat with the wax composition, described below. Lengths of 1.5 inches are suitable and generally last for 15 determinations before they become too short.

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[123] J. O. Clarke, *J. Assoc. Official Agr. Chem., 11,* 438 (1938).

[124] N. I. Goldstone, *Ind. Eng. Chem., Anal. Ed., 18,* 797 (1946).

Rub some magnesium carbonate into gum arabic paste, coat the plane ends of the short rods with the paste, and allow to dry. Dip one end of the short rods into a beaker of molten wax prepared from three parts of paraffin and one part of Acrowax C, withdraw, allow to harden, and repeat the operation on the other end of the rod, covering the entire surface with a layer of wax about $^1/_{16}$ inch thick. It may be necessary to repeat the coating in order to get it sufficiently thick. Scrape the plane ends free of the wax and soak in water to remove the paste coating. Activate the uncoated ends of the rods with stannous chloride, as directed above, and store under water acidified with a drop of concentrated hydrochloric acid. Since after each arsenic determination the plane surfaces remain activated, the initial activation is the only one necessary. As the zinc is dissolved during a series of determinations, the protruding collar of wax should be scraped off.

c. Molybdenum Blue Method[125–133]

The molybdenum blue method for the estimation of arsenic is one of the most sensitive methods that can be used for this purpose. Phosphorus reacts with ammonium molybdate to form a complex molybdiphosphate. This may subsequently be reduced with the formation of a complex molydenum compound strongly colored blue. Arsenic undergoes an entirely analogous reaction with the formation of an intensely colored blue complex. This reaction of arsenic and its use in methods for the estimation of arsenic have been discussed by a number of investigators.

The arsenic is put into solution by methods previously detailed. It is evolved as arsine, which is trapped and oxidized by bromine water or

[125] G. Deniges, *Compt. rend., 171,* 802 (1920).

[126] W. R. G. Atkins and E. G. Wilson, *Biochem. J., 20,* 1225 (1926).

[127] E. H. Maechling and F. B. Flinn, *J. Lab. Clin. Med., 15,* 779 (1930).

[128] R. B. Deemer and J. A. Schricker, *J. Assoc. Official Agr. Chem., 16,* 226 (1933).

[129] C. Zinzadze, *Ind. Eng. Chem., Anal. Ed., 7,* 227, 230 (1935).

[130] F. D. Snell and C. T. Snell, *Colorimetric Methods of Analysis*, Van Nostrand, New York, 1936.

[131] A. L. Chaney and H. J. Magnuson, *Ind. Eng. Chem., Anal. Ed., 12,* 691 (1940).

[132] Morris B. Jacobs and J. Nagler, *Ind. Eng. Chem., Anal. Ed., 14,* 442 (1942).

[133] C. C. Ruchoft, O. R. Placak, and S. Schott, *U. S. Pub. Health Service, Reprint* ***2527*** (1943).

by sodium hypobromite solution. Ammonium molybdate is added, and the color of molybdenum blue is developed by the use of hydrazine sulfate, $N_2H_4.H_2SO_4$.

Procedure. Make an acid digestion of the material to be analyzed as directed on page 235. Prepare a Gutzeit generator in the usual way (page 237); however, instead of the tube containing the mercuric bromide test paper, attach another tube leading the generated gases to a trapping device containing 3 ml. of sodium hypobromite solution (3 ml. half-saturated bromine water plus 1 ml. 0.5 *N* sodium hydroxide solution), as shown in Figure 82, or use two ordinary small gas-washing devices. It is better to have two trapping devices in series, and the second need contain only water. Treat the arsenic test solution in the same way as in the Gutzeit method.

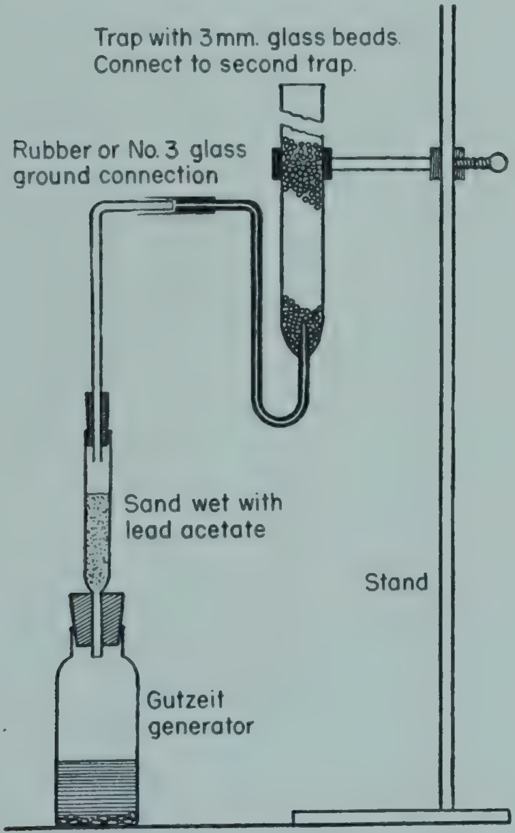
Trap with 3mm. glass beads.
Connect to second trap.
Rubber or No. 3 glass ground connection
Sand wet with lead acetate
Stand
Gutzeit generator

Fig. 82. Apparatus for arsine-molybdenum blue method.

Allow the generation of arsine to proceed as directed in the Gutzeit method. After generation is complete, transfer the contents of the traps to a graduated colorimeter tube, Nessler tube, or volumetric flask. Wash the trap with six 2-ml. portions of water, delivering the water to the trapping device with a 2-ml. pipette. Use a rubber-bulb aspirator to blow the wash solutions out of the trap into the collection vessel. Press the aspirator bulb gently in this step. Add exactly 5 ml. of 2 *N* sulfuric acid and stir; add 1 ml. of ammonium molybdate reagent (page 347) and shake. Add 1 ml. of the half-saturated hydrazine sulfate solution and swirl, make to a volume of 25 ml., and allow to stand for 0.5 hour for full development of the blue color. Compare with standards or a standard treated in a similar way at the same time.

Preparation of Standards. Prepare the standards or standard from the diluted stock standard arsenious oxide solution (page 243). Add 3 ml. of sodium hypobromite solution to the aliquot or aliquots selected, dilute to 15 ml. with water, add exactly 5 ml. of 2 *N* sulfuric acid, and stir. Add 1 ml. of the molybdate reagent, stir, add 1 ml. of half-saturated hydrazine sulfate solution, and stir. Make up to the same volume as the test solution. Run a blank on all the reagents as a check.

If a final volume of 25 ml. is to be used in making the comparisons, use exactly 5 ml. of 2 *N* sulfuric acid, in order to have the proper acidity for the development of the molybdenum blue color. If less than this quantity of acid is used, the blank may itself be reduced. If more than this quantity of acid is used, the development of the blue complex will be delayed.

The method may be used directly for the determination of arsine in industrial air by trapping in hypobromite solution, provided no phosphates or phosphorus compounds are present along with the arsine.

d. Bromate Method[134]

The bromate method for the determination of arsenic is applicable when the amount of arsenic trioxide to be estimated is of the order of 0.35 mg. The method is based on placing the arsenic into solution by means of the wet method, or acid digestion. Then the arsenic is distilled as arsenious chloride, $AsCl_3$, along with hydrogen chloride. The distillate is titrated with standard bromate solution using methyl orange as indicator.

The distillation apparatus (Fig. 83) consists of an 800-ml. Kjeldahl flask, a tube, and a 300-ml. wide-mouth flask. To make the tube, bend a 10–15 mm. glass tube to an acute angle of about 70°. Draw the longer arm, which is about 15–20 inches long, down to an orifice of about 3 mm. Fit the shorter arm, which is about 4 inches long, with a rubber stopper, which has previously been boiled in 10 per cent sodium hydroxide solution for about 15 minutes, and then in hydrochloric acid for 15 minutes in order to remove most of the sulfur compounds which might be distilled and react with the bromate solution.

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[134] *Methods Assoc. Official Agr. Chemists,* 6th ed., 1945.

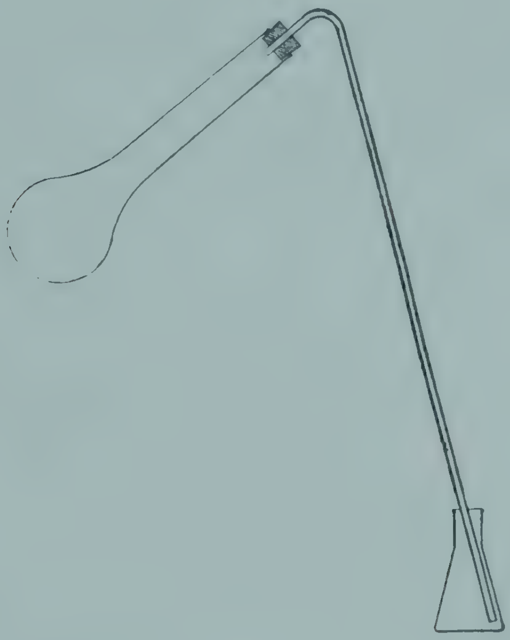

Fig. 83. Distillation apparatus for determination of arsenic by the bromate method.

Preparation of Reagents. Standard Potassium Bromate Solution. Dissolve 0.1823 g. of potassium bromate, $KBrO_3$, in water and dilute to 1 liter. One ml. of this solution is equivalent to 0.324 mg. of arsenic trioxide, As_2O_3. Standardize by titration against standard arsenious oxide solution, making the titration at about 90° C. and in the presence of about 100 ml. of water and 25 ml. of hydrochloric acid, in order to simulate the conditions under which the unknown samples will be titrated. One ml. of the bromate solution should be equivalent to 1 ml. of the arsenious oxide solution.

Standard Arsenious Oxide Solution. Dissolve 0.3241 g. of arsenic trioxide, As_2O_3, in 25 ml. of 10 per cent sodium hydroxide solution, make slightly acid with sulfuric acid (1:6), and dilute with water to 1 liter.

Hydrazine Sulfate-Sodium Bromide Solution. Dissolve 20 g. of hydrazine sulfate and 20 g. of sodium bromide in 1 liter of hydrochloric acid (1:4).

Method. Proceed with the wet-ash digestion using exactly 20 or 25 ml. of concentrated sulfuric acid at the beginning of the digestion. After the digestion is complete, add 50 ml. of water and 25 ml. of saturated ammonium oxalate solution containing 50 g. of urea per liter, and boil until white sulfur trioxide fumes extend up into the neck of the flask to decompose oxalates and urea completely.

Add 25 ml. of water and cool to room temperature. Place 100 ml. of water into the

300-ml., wide-mouth flask. Add to the mixture in the Kjeldahl flask 20 g. of sodium chloride, not iodized, and 25 ml. of the hydrazine sulfate-sodium bromide solution. Connect the distilling apparatus. Heat the Kjeldahl flask over a small well-protected flame and catch the distillate in the water in the wide-mouth flask. The heating generates hydrogen chloride gas, which carries over the arsenious chloride with it. The absorption of the evolved hydrogen chloride gas by the water causes a rise in temperature, by means of which rise the progress of the distillation can be followed. Adjust the flame so that the temperature of the distillate solution will rise to 90° C. in 9–11 minutes, and then discontinue the distillation. The residual mixture in the Kjeldahl flask should not be less than 55 ml. If the distillation proceeds further, or a larger quantity of sulfuric acid than that specified is used in the digestion, sulfur dioxide may be distilled. This is titrated as arsenious oxide.

Titrate the distillate at once with the bromate solution, using 3 drops of methyl orange indicator. Single drops of indicator, but not exceeding 3, may be added during titration as the red color fades. Toward the end of the titration add the bromate solution very slowly and with constant agitation to prevent local excess. The end point is reached when a single drop of the bromate just destroys the final tinge of red color. To determine when this point has been reached use a similar wide-mouth flask of clear water for comparison. The end point must not be exceeded, as the action of the indicator is not reversible and back titrations are not reliable. At the proper end point, the red color produced by 2 additional drops of methyl orange indicator should persist for at least 1 minute. Correct the results for the volume of bromate used in a blank determination using 5 g. of pure sucrose and the same quantities of reagents, as well as the same distillation procedure. The blank titration should not exceed 0.7 ml. of bromate solution and variations in the blank should not exceed 0.1 ml. when chemicals from the same lot are used. If doubt arises, run a Gutzeit determination on an aliquot.

e. Other Methods

Iodometric Method. Cassil and Wichmann[135] describe a rapid volumetric method for the determination of arsenic in microgram quantities. An acid digestion is performed on the material. Then the arsenic is evolved in a special generator as arsine, which is trapped in a mercuric chloride solution contained in a special tube made of methyl methacrylate resin. The liberated arsine is absorbed quantitatively by the mercuric chloride solution, forming mercury arsenides. The arsenides are oxidized by the excess mercuric chloride with the formation of mercurous chloride and arsenious acid. The arsenious acid may then be oxidized to arsenic acid with 0.001 *N* iodine solution.

Chlorometric Method. Arsenic may also be determined by chlorometry, using the method of Goldstone and Jacobs[136] as detailed on page 257 for the estimation of antimony.

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[135] C. C. Cassil and H. J. Wichmann, *J. Assoc. Official Agr. Chem.*, 22, 436 (1939).

[136] N. I. Goldstone and Morris B. Jacobs, *Ind. Eng. Chem., Anal. Ed.*, 16, 206 (1944).

6. *Arsine*

Arsine—arseniureted hydrogen, hydrogen arsenide, arsenic trihydride, AsH_3—occurs in potentially dangerous concentrations in many industries, among which may be mentioned the manufacture of zinc chloride and sulfate, the smelting of arsenical and arsenic-bearing ores, the manufacture of enamel ware, dyestuffs and dyestuff intermediates, electroplating and galvanizing works, the production of hydrochloric and sulfuric acids, and, in general, wherever hydrogen is evolved there is also the possibility of evolution of arsine.

Several deaths and injuries occurred in 1949 from arsine apparently resulting from the presence of an aluminum arsenide in some metal dross where aluminum was used in the drossing process.[136a]

Arsine is a colorless gas with an extremely offensive odor resembling that of garlic. It is 2.7 times as heavy as air. It is somewhat soluble in water but is insoluble in ether and alcohol. It decomposes with heat and is inflammable.

a. Physiological Response

Arsine is a nerve and blood poison. There is generally some delay, sometimes a day or so, before the onset of symptoms. These are at first usually indefinite. There is a general feeling of malaise, difficulty in breathing, severe headache, giddiness, fainting fits, nausea, vomiting, and gastric disturbances.[137,138] In more severe cases the vomiting may be more pronounced, the mucous membranes may have a bluish discoloration, and the urine is dark or blood-stained. After a day or two there is severe anemia and jaundice.

A concentration of 500 parts per million is lethal for a man after exposure of a few minutes. A concentration of 250 parts per million, equivalent to 0.75 mg. per liter, is dangerous to life for exposure of 30 minutes. Concentrations of 6.25–15.5 parts per million, that is, 0.02–0.05 mg. per liter, are dangerous after exposure for 30 to 60 minutes. The maximum concentration tolerated for several hours without serious symptoms is 3.1 parts per million.[139] Sayers[138] gives a concentration of 10 parts per million as the concentration that can be tolerated for several hours without serious symptoms. Table 4, Appendix, gives the maximum allowable concentrations suggested by several authorities. There are no recorded figures as to the limits of concentration that may be regarded as harmless for continuous daily exposure, but there is evidence that repeated exposures to very low concentrations may have cumulative effects resulting in severe poisoning.[137] The maximum allowable concentration submitted by the Committee on Threshold Limits and accepted by the American Conference of Governmental Industrial Hygienists[140] is 0.05 part per million.

[136a] R. N. Harger, personal communication, 1949.

[137] *Dept. Sci. Ind. Research Brit., Leaflet 9* (1940); *Analyst, 65,* 354 (1940).

[138] R. R. Sayers, *International Critical Tables,* Vol. II, McGraw-Hill, New York, 1927.

[139] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

b. Detection

The official British method for the detection of arsine in air uses a mercuric chloride test paper. Although silver nitrate test paper is about 20 times as sensitive as mercuric chloride paper, it has the drawbacks that the stains vary in color from yellow to black, depending on the drying temperature; they continue to darken rapidly so that matching is difficult; and the papers do not keep well.

In the British[137] standard test, the test papers are prepared by immersing the strips of filter paper in 5 per cent mercuric chloride solution, drying them, and cutting off and discarding the ends.

The atmosphere under examination is drawn by means of a hand pump, described elsewhere, through the test paper, and the resulting stain, if any is produced, is compared within 5 minutes with the standard stains issued with the leaflet. The concentration of arsine is then found by reference to the color chart, which shows the intensities of stains corresponding with 10 to 50 strokes of the pump. In this way concentrations of arsine down to 4 parts per million, that is, 0.013 mg. per liter, can be detected. The atmosphere to be tested is passed through lead acetate paper to absorb any traces of hydrogen sulfide before coming in contact with the mercuric chloride paper.

Alternatively mercuric bromide test paper prepared as directed in the Gutzeit method may be used. The depth and intensity of the stain is indicative of the amount of arsine.

c. Determination

Arsine may be estimated quantitatively by absorption in potassium iodide solution acidified with sulfuric acid with subsequent titration of the liberated iodine. It may be determined by absorption in silver nitrate solution with subsequent titration of the resulting arsenious acid. It may be trapped in nitric acid, bromine, or other oxidizing medium and then estimated by one of the methods detailed above. Alternatively arsine may be trapped in sodium hypobromite solution and then the arsenic may be estimated by the molybdenum blue method.

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[140] *Ind. Hyg. Newsletter, 7,* No. 8, 15 (1947).

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CHAPTER VIII

Other Harmful Metals

Increase in occupational diseases in more recent years has been associated to a large extent with changes in the methods of industry. The application of chemistry to industrial processes has been the means of introducing certain new hazards to health, since in many instances the chemicals involved in the new processes are of such a nature as to constitute a source of injury unless precautionary measures are exercised.[1] Two well-known examples are the electro-deposition of chromium and the use of benzene as a solvent.

The metals discussed in the previous chapter are not only serious hazards but they are also extensive hazards in that they are industrial poisons in many different trades. The metals to be discussed in this chapter are not used as extensively in trade as are those of the previous chapter. Some of them are true poisons, such as antimony, chromium, cadmium, manganese, and selenium. Others have a deleterious effect because of their state of subdivision when inhaled, as, for instance, zinc and magnesium oxides. The metals zinc, magnesium, and nickel have not been shown to be poisonous as such. Nevertheless, they may form poisonous compounds, as, for example, zinc chloride, which is caustic, and nickel carbonyl, which is extremely poisonous.

The utilization of such metals as beryllium and cobalt and their compounds for newer purposes, such as the use of beryllium compounds for the preparation of fluorescent powders and fluorescent lamps and of cobalt carbonyl as a catalyst in the manufacture of motor fuels, are accompanied by hazards not heretofore encountered.

A. CHROMIUM

It has generally been recognized that the spray of chromic acid produced during the process of plating is injurious to workers. Practically all of the chromium-plating baths now used have chromic acid as their principal component, which may be present in concentrations from 200 to 500 g. per liter (27 to 67 ounces per gallon). In addition there are present small amounts of some other anion such as sulfate, introduced either as the sulfate of a salt or as sulfuric acid. Variable amounts of trivalent chromium and trivalent iron, which is derived from the iron tanks or anodes, are also likely to be present in used baths, either in true or in colloidal solution. Lead anodes are generally employed, which produce at least small amounts of lead chromate and peroxide upon their surfaces and possibly in suspension in the baths. Oxygen is evolved on the insoluble anodes and considerable hydrogen is liberated on the cathodes. These gases tend to carry a fine mist or spray of the liquid present in the tank into the surrounding air. The injurious component is deemed to be the chromic acid.

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[1] J. J. Bloomfield and W. Blum, *U. S. Pub. Health Repts., 43,* 2330 (1928).

Injuries from chromates have been known for over 100 years. They occur, generally, in the form of ulcers known as "chrome holes." Continuous daily exposure to concentrations of chromic acid greater than 1 mg. per 10 cubic meters is likely to cause definite injury to the nasal tissue of workers.[2] This concentration is the recommended maximum allowable concentration. Contact with abrasions in the skin is also dangerous. Chromates also cause severe kidney damage and intestinal inflammation. Chromium may also be a hazard in welding operations.

1. Sampling

Sampling the atmosphere for chromic acid spray may be accomplished with the Greenburg-Smith impinger device or with one of its modifications by drawing the air through 200 ml. of *N* sodium hydroxide solution. The rubber stoppers holding the impinging device in the collecting vessel should be coated with paraffin to eliminate the action of chromic acid vapor on the rubber. The amount to be sampled depends on conditions. From 20 to 165 cubic feet (0.5 to 5 cubic meters) of air should be sampled, according to the chromic acid concentration. Samples should be taken to simulate working conditions—for instance, above the plating baths, near the point where the operator stands, and at breathing level. The amount of air sampled is obtained, as usual, by use of an appropriate gas-flow measurement device; for example, if compressed air is available, by use of the Hatch ejector vacuum gauge, described on page 67. Other absorber sampling devices may be used, as, for instance, the type which passes the air through a sintered-glass plate at the bottom of an absorption flask and thus makes intimate contact with the alkali absorbing solution, or those which dispense with solutions and trap the chromic acid in or on a filter. All-glass impingers are also useful.

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[2] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem.*, 26, 1251 (1934).

2. *Determination*

a. Iodide-Thiosulfate Method

Potassium iodide is added to an aliquot of the alkaline solution from the absorption bottle or to a prepared solution from one of the other sampling methods. The solution is then acidified with hydrochloric acid or sulfuric acid and the liberated iodine is titrated with standard 0.01 *N* sodium thiosulfate solution, using starch as an indicator.

Make the alkaline chromate solution nearly acid with sulfuric acid. If necessary, boil the solution with 20 ml. of 30 per cent potassium hydrogen sulfate solution to expel hydrogen peroxide or oxygen. Transfer to a glass-stoppered bottle. Wash and make the solution just acid with sulfuric acid and if the chromate is of the order of 0.1 g., add 1 ml. of sulfuric acid in excess or correspondingly less. Add 0.2 to 0.5 g. of potassium iodide, according to the amount of chromate, stopper the flask, and after 5 minutes titrate the liberated iodine with 0.01 *N* sodium thiosulfate solution. When the green color of the reduced chromate begins to predominate over the brownish-red of the free iodine, add 0.5 ml. of 1 per cent starch solution and continue with the titration until the blue color of the starch is discharged. Care must be taken not to confuse the green color of the reduced chromium with the blue of the starch-iodine complex. One ml. of 0.01 *N* sodium thiosulfate solution is equivalent to 0.0001733 g. of chromium.

b. Hematoxylin Method[3]

As an additional check for very small amounts of chromium, Bloomfield and Blum[4] suggest the hematoxylin method. To a 5-ml. aliquot portion of the alkaline absorbing solution add 1 drop of methyl red and acidify with acetic acid to a faint yellow, pH about 6. Add one drop of a 1 per cent aqueous solution of hematoxylin and bring the solution to boiling. A distinct violet coloration appears with even traces of chromic acid. By comparison with the color produced with aliquots of a stock standard solution of bichromate, it is possible to detect and estimate as little as 0.01 mg. of chromic acid, CrO_3, in a 5-ml. aliquot of the sample solution.

[3] F. Vogel, *Z. anal. Chem.*, *2*, 390 (1863).
[4] J. J. Bloomfield and W. Blum, *U. S. Pub. Health Service, Reprint 1245* (1928).

The concentration of chromic acid should be expressed in mg. per cubic meter to conform with literature references.

c. *s*-Diphenylcarbazide Method[5]

The industrial hazards of chromium compounds are not all attributable to the vapor of chromic acid and it is at times necessary to trap the chromium-bearing dust, mist, and spray on filters. If the chromium is not in the chromic state it will not be estimated by the aforementioned methods unless it is first oxidized to that state. The following method overcomes some of these difficulties.

The chromium compounds are trapped by filtration and the sample is ashed. The chromium is then oxidized to chromate by hydrogen peroxide in alkaline solution. It is then separated from other metals by precipitation as lead chromate with lead acetate. The filtered precipitate is then dissolved in hydrochloric acid and the acid chromate is compared with standard solutions of potassium chromate, using *s*-diphenylcarbazide.

Trap the chromium compounds in the air by drawing the air through a glass bulb containing two cotton filter plugs moistened with a little glycerol. Note the volume of air drawn through. Three liters may be sufficient. Ash the plugs in a procelain dish at low red heat. Cool, and completely dissolve the ash in dilute hydrochloric acid with the aid of gentle heat. If too high a temperature was used in ashing and any insoluble material is left, it is necessary to put this material into solution with sodium peroxide. Take the hydrochloric acid solution to dryness two or three times with concentrated nitric acid, in order to remove all hydrochloric acid, and finally dissolve the residue in dilute nitric acid. Neutralize with potassium hydroxide solution, adding a slight excess, and then add 5 ml. of concentrated hydrogen peroxide. Heat and boil off the excess peroxide. Since the metal hydroxides precipitated by this treatment retain some of the chromium mechanically, it is necessary to filter and dissolve the residue in dilute nitric acid, neutralize again, and oxidize again with concentrated hydrogen peroxide. A third oxidation serves to remove every trace of chromium from the insoluble components of the ash.

Combine the filtrates, neutralize with acetic acid, and add a slight excess of this acid. Add lead acetate solution and precipitate lead chromate. Insoluble lead phosphate may also precipitate at this point but will not interfere with the subsequent analysis. Filter. Dissolve the well-washed lead chromate precipitate in hydrochloric acid. Transfer the solution to a volumetric flask and make to volume. The chromium content may now be estimated by comparison against standard potassium chromate solutions in the same strength hydrochloric acid in a colorimeter or in 50-ml. Nessler tubes.

The *s*-diphenylcarbazide reagent is best prepared by dissolving 0.4 g. of the chemical in 30 ml. of glacial acetic acid and diluting to 400 ml. with water. Add 1 ml. of this 0.1 per cent solution of *s*-diphenylcarbazide to the standard and test solution in Nessler tubes. Wash down the walls with water. Mix the contents thoroughly and allow to stand for 15 minutes. Make to volume with water. The quantities of chromium that can be read with the greatest accuracy vary from 0.003 mg. to 0.01 mg. of chromium in a 50-ml. Nessler tube, with 0.007 mg. the optimum amount.

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[5] K. Akatsuka and L. T. Fairhall, *J. Ind. Hyg.*, *16*, 1 (1934).

B. ANTIMONY

Antimony is an industrial hazard mainly in three industries. In the rubber industry, golden and crimson antimony sulfides are used as pigments.[6] In the printers' trade, type metal contains antimony. Antimony is also a hazard in the storage-battery industry, where it is used for grids as an alloy of lead and antimony. In all of these industries, much lead is also used and it is difficult to give the proper degree of hazard to antimony alone. That it is poisonous is sufficiently clear from food poisonings attributable to antimony-contaminated enamel cooking utensils. Antimony resembles arsenic in its action on the human system. The literature concerning the toxicology of antimony has been comprehensively reviewed by Fairhall and Hyslop.[7] The recommended maximum allowable concentration of antimony is 0.1 mg. per cubic meter of air.

It is the opinion of the author that some of the published work concerning the analytical recovery of antimony is unreliable. It has been shown[8] that antimony is lost as antimony pentachloride, $SbCl_5$, when hydrochloric acid solutions of antimony are boiled. Antimony chlorides behave differently than arsenic chlorides. Thus the lower valent arsenious chloride, $AsCl_3$, boils at a lower temperature (130.2° C.) than the higher valent arsenic pentachloride; whereas the lower valent antimonious chloride, $SbCl_3$, boils at a higher temperature (223° C.) than the corresponding higher valent antimony pentachloride, $SbCl_5$, boiling at 140° C. The pentachloride dissociates slowly at its boiling temperature, yielding free chlorine and the trichloride. The trichloride has an appreciable volatilization in hydrochloric acid solutions at temperatures as low as 110° C.

Some investigators use the acid-digestion method for the recovery of antimony from organic materials, from mixtures with organic materials, and to free it from the cellulosic materials used to trap the fume or dust while sampling. Goldstone[9] and also Jacobs[10] have shown that antimony is "lost" in any acid digestion containing an oxidizing medium such as nitric acid, hydrogen peroxide, etc., or when acid solutions of antimony containing an oxidizing substance such as nitric acid, chlorine, bromine, or hydrogen peroxide are boiled or evaporated.

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[6] R. S. Quinby, *J. Ind. Hyg.*, *8*, 103 (1926).

[7] L. T. Fairhall and F. Hyslop, *U. S. Pub. Health Repts., Supplement 195* (1947).

[8] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929.

Maren[11] pointed out that an investigation of the valency state of antimony following a typical sulfuric acid-nitric acid digestion showed that about 35 per cent was in the trivalent state, 15 per cent was in the quinquevalent state, and 50 per cent was apparently "lost," that is, was in neither the trivalent nor quinquevalent state. It was shown many years ago that nitric acid oxidation of antimony is never complete to the quinquevalent state[12] and that there is evidence of a quadrivalent antimony.[13]

These sources of error must be taken into consideration in using any procedure for the determination of antimony.

Determination and Detection

Where other metals are present in negligible amounts, antimony-bearing dust may be trapped by one of the devices previously described and may be subsequently estimated by the sulfide method. The midget impinger has been recommended for antimony dusts.

Antimony may be detected qualitatively by the Reinsch test, as detailed for arsenic (Chapter VII, Section C5). Bamford[14] describes a method in which antimony is thrown down as the sulfide and is then determined colorimetrically against standards prepared in a similar manner.

a. Sulfide Method

If necessary, ash the sample, using a few ml. of a saturated solution of magnesium nitrate, $Mg(NO_3)_2$, to fix the antimony. Use ammonium nitrate to obtain a clean ash, if needed, and reheat until free of nitrates. Dissolve the ash when cold in sufficient hydrochloric acid and water to give a definitely acid reaction.

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[9] N. I. Goldstone, personal communication of unpublished work to the author (1940).
[10] Morris B. Jacobs, unpublished work (1940).
[11] T. H. Maren, *Bull. Johns Hopkins Hosp., 77,* 338 (1945); *Anal. Chem., 19,* 487 (1947).
[12] C. P. Conrad, *Chem. News, 40,* 197 (1879).
[13] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry.* Vol. IX, Longmans, Green, London, 1929.
[14] F. Bamford, *Analyst, 59,* 101 (1934).

Dilute the solution with water and treat with hydrogen sulfide. Filter off the precipitate, wash in the usual way, and dissolve in a minimum quantity of hot concentrated hydrochloric acid. Dilute this solution with water, refilter, add 1 ml. of a 5 per cent solution of gum ghatti or gum arabic per 100 ml. of the liquid to hold the precipitated antimony sulfide in suspension, and make the solution up to a definite volume. Pass in hydrogen sulfide again and compare the color produced with that of a standard of approximately equal concentration with the aid of a colorimeter, or transfer to a Nessler tube and compare with standards in similar tubes.

Preparation of Standard. The standard may be prepared by diluting 1 ml. of a 5 per cent tartar emetic solution [potassium antimonyl tartrate, $2K(SbO)C_4H_4O_6.H_2O$], slightly acid and mixed with gum arabic or gum ghatti solution, to 1 liter. An appropriate aliquot is then treated with sufficient gum solution to give the same concentration as that in the unknown and is made up to definite volume. It is then saturated with hydrogen sulfide and used as the standard.

Separation from Interferences. Where the antimony-bearing dust is also lead bearing, the metals must be separated before estimation of the antimony can proceed. This may be done by the usual polysulfide method. Prepare a solution of the sample as described under lead. Pass in hydrogen sulfide until the solution is saturated. Add an equal volume of water and again saturate the solution. Filter the sulfides preferably through a sintered-glass filter such as a Jena-glass filter No. 11 GA or an equivalent Pyrex type. Dissolve the antimony and any tin, if present, with five applications of 5 ml. each of warm polysulfide reagent, prepared as directed under the Wichmann-Clifford method for lead (Chapter VII, Section A3e). Wash the filter four times with 3 per cent sodium sulfate solution, 3 g. of anhydrous sodium sulfate, Na_2SO_4, in 100 ml. of water. Combine all the polysulfide filtrates and the wash solutions. The precipitate on the filter may be estimated for lead as described. Neutralize the combined filtrates slowly with hydrochloric acid, dilute, adding the acid dropwise near the neutral point, finally add 2 ml. of dilute acid in excess. Filter off the precipitate. Redissolve in a minimum quantity of hot concentrated hydrochloric acid. Dilute with water and filter if necessary. From this point, if tin is not present, proceed as directed above, estimating antimony sulfide in the presence of a stabilizing gum, or use the following bromate method.

If tin is present, the sulfides are dissolved in concentrated sulfuric acid, the tin forming a stannic compound and the antimony forming an antimonious compound. By the use of a standard solution of potassium permanganate, the antimonious ion may be oxidized to the antimonic ion, the amount of antimony being estimated from the relationship that

$$5Sb_2(SO_4)_3 + 4KMnO_4 + 24H_2O \longrightarrow 10H_3SbO_4 + 2K_2SO_4 + 9H_2SO_4 + 4MnSO_4$$

Tin may subsequently be estimated by reducing it to the stannous form by heating with antimony metal and subsequently titrating with standard iodine solution, which oxidizes the tin back to the stannic form.

$$SnCl_2 + 4HCl + I_2 \longrightarrow H_2SnCl_6 + 2HI$$

b. Bromate Method[15]

In this method antimony is precipitated as the sulfide. It is separated from interferences by the use of polysulfide and then is reprecipitated as the sulfide. After dissolving the sulfide in concentrated hydrochloric acid, the antimony is reduced to the antimonious state by means of sulfite and is estimated by oxidation to the antimonic state by standard bromate solution.

Place the sample in a porcelain crucible, add 1 ml. of saturated sodium carbonate solution and 0.5 g. of magnesium oxide. Dry the mixture in an oven and carefully ash at low red heat, first over a low flame and finally in a muffle oven. Dissolve the ash in 25 ml. of hot, dilute hydrochloric acid. Filter the solution and wash the crucible and filter paper, catching the filtrate and washings in a wide-mouth flask. Pass hydrogen sulfide gas through the solution for 0.5 hour and allow the precipitate to settle overnight. Then filter through paper and wash with hydrogen sulfide water. Return the precipitate with the filter paper to the flask and warm with a solution of sodium polysulfide. Filter and wash well with hot water, catching the filtrate and washings in a 250-ml. beaker. Acidify the filtrate with hydrochloric acid and again allow to stand overnight. Filter the precipitate through a Gooch crucible equipped with an asbestos mat and wash with hydrogen sulfide water. Place the Gooch crucible back into the precipitation beaker; break up the asbestos mat with a glass rod and dissolve the sulfide in 20 ml. of boiling hydrochloric acid (1:1). Filter and wash with hot water. Evaporate the filtrate to a volume less than 50 ml. Transfer to a 50-ml. volumetric flask and make to volume.

Transfer an aliquot portion of this solution to a 100-ml. Erlenmeyer flask. Add 5 ml. of concentrated hydrochloric acid and 20 mg. of sodium sulfite. Boil the solution to remove the sulfite. Titrate the hot solution with 0.005 *N* potassium bromate solution (0.1392 g. $KBrO_3$ dissolved in water and made up to 1 liter) with a micro- or semimicroburette, using 2–3 drops of 1 per cent methyl orange solution as indicator. One ml. of 0.005 *N* potassium bromate solution is equivalent to 0.3044 mg. of antimony. Run a blank determination. The blank titration should not exceed 0.3 ml. of 0.005 *N* potassium bromate solution.

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[15] C. W. Anderson, *Ind. Eng. Chem., Anal. Ed.*, *11*, 224 (1939).

c. Chlorometric Method[16]

"Chlorometry" is the term used to designate the quantitative estimation of various substances by use of a standard hypochlorite solution, in a manner entirely analogous to iodometry and bromometry. It is a popular misconception that because sodium hypochlorite is a highly reactive substance it is too unstable to be used as a standard titrimetric reagent. Undoubtedly one reason for the lack of enthusiasm among analysts for the use of sodium hypochlorite as a titrimetric reagent is the apparent difficulty of preparing such solutions. It may be prepared in the following simple manner.

Preparation of Standard Sodium Hypochlorite Solution. Transfer 8.0 ml. of a commercial preparation of sodium hypochlorite solution containing 5 per cent of available chlorine to a glass-stoppered brown-glass bottle, and dilute with water to about 2 liters. If necessary, add sufficient sodium hydroxide (1 g.) to raise the pH to about 12.5, the optimum pH for stability. To ascertain if the proper pH has been reached, the customary colorimetric methods for the determination of pH in the range 12 to 14 may be used. Obtain the titer of the solution by titration against a primary standard of sodium arsenite made as follows:

Weigh 0.2473 g. of arsenious oxide (arsenic trioxide, As_2O_3, National Bureau of Standards) and dissolve in 25 ml. of 10 per cent sodium hydroxide solution. Transfer to a 1-liter volumetric flask, make slightly acid with sulfuric acid (1 to 6), and dilute with water to 1 liter. This solution is 0.005 *N*.

The solution of sodium hypochlorite made as directed above is generally somewhat stronger than 0.005 *N*. Its exact titer can be determined by titration against the standard arsenite solution. Its normality may be adjusted to exactly 0.005 *N* by the usual procedure.

Titrimetric Procedure. Transfer a known aliquot of standard arsenite solution to a 125-ml. Erlenmeyer flask or a 150-ml. beaker: a 4-ml. aliquot if a microburette is to be used for the standard hypochlorite solution and a 5-ml. aliquot if a semimicroburette is to be used. A standard solution of tartar emetic [potassium antimonyl tartrate, $2K(SbO)C_4H_4O_6H_2O$] containing 1 mg. of antimony per 10 ml. of solution may also be used. Add 5 ml. of concentrated hydrochloric acid and adjust the volume of the solution to 35 to 40 ml. by adding distilled water. Fill a micro- or semimicroburette with the standard hypochlorite solution. Add 1 drop of 0.05 per cent methyl orange indicator solution to the test solution and titrate directly with the sodium hypochlorite solution. Add another drop of methyl orange indicator solution near the end point and continue the titration until the color of the methyl orange is destroyed. Make a blank titration using exactly the same volume of hydrochloric acid, water, and 2 drops of methyl orange indicator solution, replacing the volume of arsenite or antimony test solution by additional distilled water. The blank should run about 0.12 to 0.14 ml.

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[16] N. I. Goldstone and Morris B. Jacobs, *Ind. Eng. Chem., Anal. Ed., 16,* 206 (1944).

Antimony solutions prepared from samples treated as described in previous paragraphs, particularly on page 255, may be estimated titrimetrically as detailed above.

Several precautions must, however, be observed in using sodium hypochlorite solution as a titrimetric reagent. It must be preserved in brown, glass-stoppered bottles. It may be kept at room temperature without deterioration over considerable periods of time. Keeping the solution at lower temperatures is perhaps preferable.

The optimum conditions for the titrations are a volume of at least 35 to 40 ml. with an acid concentration equivalent to 5 ml. of concentrated hydrochloric acid.

d. Rhodamine B Colorimetric Method[17-20]

In this method all the antimony in the intermediate or unreactive state (see page 254) is either oxidized to the quinquevalent state by use of perchloric acid at the end of the digestion, or is reduced to trivalent antimony by sulfur dioxide following the destruction of organic matter by the acid digestion and subsequently oxidized to the quinquevalent state by ceric sulfate in the presence of hydrochloric acid. A lake is prepared using rhodamine B; this lake is extracted by a suitable solvent, and the color is estimated colorimetrically or photometrically. If perchloric acid is used in the digestion,[21] it is not necessary to use the sulfur dioxide reduction or the ceric sulfate oxidation.

Procedure. Add 2 drops of 60 per cent perchloric acid to the water-white acid digest and heat until fumes of sulfur trioxide are evolved. If charring or yellowing occurs, it is necessary to add additional perchloric acid but not over a total of 0.5 ml. when 10 ml. of 18 *N* sulfuric acid is used

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[17] W. G. Fredrick, *Ind. Eng. Chem., Anal. Ed., 13,* 992 (1941).

[18] T. H. Maren, *Bull. Johns Hopkins Hosp., 77,* 338 (1945).

[19] T. H. Maren, *Anal. Chem., 19,* 487 (1947).

[20] S. H. Webster and L. T. Fairhall, *J. Ind. Hyg. Toxicol., 27,* 183 (1945).

[21] L. D. Freedman, *Anal. Chem., 19,* 502 (1947).

initially. Cool, add 3 ml. of water, and heat until fumes are evolved. Cool again and place in a cold-water bath. Add 5 ml. of 6 *N* hydrochloric acid.

Benzene Extraction. Add 8 ml. of 3 *N* phosphoric acid, 70 ml. of concentrated acid diluted to 1 liter, and 5 ml. of 0.02 per cent rhodamine B solution, 0.20 g. of the dye dissolved in water and diluted to 1 liter. Shake the flask and cool again if necessary. The benzene extraction must now be performed without delay. Transfer to a separatory funnel. Rinse the digestion flask with 10 ml. of benzene and transfer the benzene to the separatory funnel. Shake 150–200 times, draw off the lower aqueous layer, and transfer the benzene phase to a tube. Allow to stand and settle. The color is stable at this point. Transfer 6 to 8 ml. to a cuvette and read at 565 mμ or use a green filter.

Isopropyl Ether Extraction. After the addition of the hydrochloric acid add 13 ml. of water and transfer to a separatory funnel. Add 15 ml. of isopropyl ether to the digestion flask, rinse, and transfer to the separatory funnel. Shake about 100 times, discard the aqueous layer. Add 5 ml. of 0.02 per cent rhodamine B solution. Shake again 150 times and after settling, discard the aqueous layer. Transfer the ether layer to a tube. Read immediately at 545 mμ or use a green filter.

Standard Solutions. Weigh accurately 0.1000 g. of chemically pure antimony and add 25 ml. of concentrated sulfuric acid. Heat until the metal dissolves. Cool and dilute to 1 liter. It is stable and contains 100 micrograms of antimony per ml. It can be diluted to give working standards.

In preparing a standard curve, add known amounts of antimony up to 40 micrograms to 5 ml. of sulfuric acid. Make an acid digestion with nitric acid. Treat with perchloric acid as detailed and then proceed with the remainder of the analysis.

Stibine

Stibine, antimony hydride, SbH_3, is a colorless, poisonous gas having an unpleasant odor. It weighs about 5.3 g. per liter. In the liquid state, it boils at −17° C. About 20 ml. of the gas is soluble in 100 ml. of cold water and much less is soluble in hot water.

Stibine is a powerful hemolytic agent[22] and its order of toxicity is similar to that of arsine.[23] Cats and dogs are readily affected, for a single exposure to concentrations of the order of 40–45 ppm. for 1 hour is dangerous. The recommended maximum allowable concentration is 0.1 part per million parts of air.

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[22] S. H. Webster, *J. Ind. Hyg. Toxicol., 28,* 167 (1946).

[23] A. Stock and O. Guttmann, *Ber., 37,* 885 (1904).

The toxicology of the volatile hydrides as a group has been discussed by Webster.

Detection and Determination

Stibine may be detected in a manner analogous to arsine by thermal decomposition. Webster and Fairhall[24] used filter paper impregnated with silver nitrate for the detection and semiquantitative determination of stibine.

Dip strips of Whatman No. 1 filter paper, 1 by 7 cm., into a 1 per cent solution of silver nitrate, allow to drain, and wave in the atmosphere for 1 minute. A brown coloration is produced, the intensity of which is proportional to the amount of gas present. Compare with standards made previously. Other hydrides such as hydrogen sulfide, arsine, hydrogen selenide, etc., and phosphorus will affect such papers. They are not stable to light.

To prepare standards, expose strips of bromide enlarging paper to light for varying lengths of time, develop, and tone in a copper bath. Match these strips with the stain produced by exposing silver nitrate papers to known concentrations of stibine, and make a color chart.

Rhodamine B Method. By use of a modification of the rhodamine B method,[24] stibine may be estimated. The gas is trapped in mercuric chloride solution, trivalent antimony is oxidized to quinquevalent antimony by ceric sulfate in the presence of hydrochloric acid, excess ceric sulfate is removed by hydroxylamine hydrochloride, and the remainder of the method follows lines previously detailed.

Procedure. Trap the gas by passing it through a bubbler containing 20 ml. of mercuric chloride solution, prepared by dissolving 60 g. of mercuric chloride, $HgCl_2$, in 6 N hydrochloric acid and diluting to 1 liter with the same acid. Transfer the trapping solution to a dry, 50-ml., glass-stoppered, graduated cylinder. Rinse the bubbler, both inside and out, and then the tube with 9 ml. of 6 N hydrochloric acid and add the washings to the cylinder. Allow to drain and complete the volume to 30 ml. Transfer 15.0 ml. with the acid of a pipette and a safety pipetter to a 125-ml. conical beaker. Add 0.5 ml. of 0.1 N ceric sulfate solution, prepared by dissolving 33 g. of anhydrous ceric sulfate, $Ce(HSO_4)_4$, in 3 per cent sulfuric acid and diluting to 1 liter. Set a timer for 1 minute and mix. At the end of this time blow clean air into the beaker for 5–10 seconds to remove free chlorine.

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[24] S. H. Webster and L. T. Fairhall, *J. Ind. Hyg. Toxicol.*, 27, 183 (1945).

Add 3 drops of 1 per cent hydroxylamine hydrochloride solution, prepared by dissolving 1 g. of hydroxylamine hydrochloride, $NH_2OH.HCl$, in water and diluting to 100 ml., and mix. Add 5 ml. of 6 N hydrochloric acid, mix, and blow out the air of the beaker with clean air to remove the last traces of chlorine. Add immediately 1 ml. of 0.2 per cent rhodamine B solution, filtering the reagent before use, mix, and transfer to a 60-ml. separatory funnel. Add 25 ml. of benzene, using 2 ml. to rinse out the beaker, and shake for 1 minute. Draw off the aqueous layer and a portion of the benzene layer. Transfer the remainder to centrifuge tubes. Centrifuge, stoppering the tubes to prevent evaporation and using pins to prevent the corks from being drawn into the tubes. Transfer to a cuvette and read the density of the color at 565 $m\mu$.

C. CADMIUM

It has been shown that cadmium is a poison entirely analogous to arsenic and mercury. It does not have a noxious effect merely because of the state of subdivision of the cadmium compounds inhaled. Cadmium melts at 320.9° C., a few degrees lower than lead. With increased use of cadmium for industrial purposes, the industrial hygienist has been presented with another problem in hygiene.[25] Among the industrial processes in which cadmium poisoning may occur are the smelting of cadmium ores, working up of residues, production of cadmium compounds, spraying of cadmium-bearing paints and pigments, welding alloys, flanging operations on cadmium-plated pipe, cadmium-plating processes, particularly of marine hardware and other fittings which were formerly zinc-coated, and melting the metal.[26]

In industry, cadmium poisoning usually occurs from the accidental absorption of cadmium fumes or dusts through the respiratory system.[26a] It seldom occurs by ingestion.

The generally accepted maximum safe permissible working concentration of cadmium fume and dust is 0.1 mg. per cubic meter, as shown in Table 6, Appendix.

Detection and Determination

A method for the detection and estimation of cadmium in air is based on the separation of cadmium from other metals as the sulfide, with its subsequent estimation by the amount of yellow color produced in a solution containing cadmium when viewed under a mercury-arc lamp.[27] In concentrations of less than 0.1 mg. of cadmium in 50 ml. of solution. differences in the yellow color of cadmium sulfide are indistinguishable in ordinary light, while under the quartz mercury-vapor lamp the yellow color is perceptible in concentrations as low as 0.01 mg. per 50 ml. of solution.

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[25] L. T. Fairhall, *Ind. Hyg. Newsletter, 6,* No. 11, 6 (1946).

[26] L. Prodan. *J. Ind. Hyg., 14,* 132, 174 (1932).

[26a] L. W. Spolyar, J. F. Keppler, and H. G. Porter, *J. Ind. Hyg. Toxicol., 26,* 232 (1944).

Cadmium dust may be trapped by means of an impinger in water, or the dust and fumes may be collected electrostatically or by filtration. Because cadmium and its salts are relatively volatile, cadmium-bearing materials are best ashed by the wet-ash method. If ignition is used, an ash aid must also be used.

Add sufficient nitric acid to the cellulosic materials or other organic material to cover them and heat gently. After the solid material has dissolved, add 10 ml. of concentrated sulfuric acid and add, when necessary, small amounts of nitric acid until oxidation is complete. The method described for arsenic may also be used. Dilute to 75 ml. and add the equivalent of 0.5 mg. of copper and 2 g. of sodium citrate. The copper is added to act as an entrainer or collector. Neutralize the acid solution for the first precipitation with ammonium hydroxide and adjust the concentration of hydrogen ion to pH 3 by means of the indicators thymol blue (thymolsulfonphthalein) and bromophenol blue (tetrabromophenolsulfonphthalein). Saturate with hydrogen sulfide solution for five to ten minutes, add 1 drop of 5 per cent aluminum chloride solution, and allow the solution to stand for 6 to 12 hours. Filter, dissolve the precipitate in nitric acid and hydrochloric acid, and carefully evaporate to dryness. Repeat the precipitation as sulfide twice more, omitting the addition of sodium citrate the last time and adjusting the pH to 2 by means of dilute potassium hydroxide. Carefully evaporate the final solution of chloride to dryness, dissolve it in water, and make up to a convenient exact volume in a volumetric flask. Transfer an aliquot portion of this prepared solution to a Nessler tube for the final reading. To each tube add 5 drops of 10 per cent potassium cyanide, water, 5 ml. of hydrogen sulfide water, and make to volume. Mix thoroughly and compare under a flood of ultraviolet light with standards similarly prepared. The solution should exhibit a bright clear yellow color under the mercury arc. Dark or turbid solutions may indicate incomplete removal of iron.

For larger quantities of cadmium, the following method may be used.

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[27] L. T. Fairhall and L. Prodan, *J. Am. Chem. Soc.*, *53*, 1321 (1931).

Neutralize the wet-ash solution, make slightly acid, but sufficiently so as to hold all the zinc in solution, and pass in hydrogen sulfide. Yellow cadmium sulfide is precipitated. If copper is present, it may be separated as follows: Redissolve the sulfides in either sulfuric or hydrochloric acid. Add an excess of sulfurous acid to make certain that no oxidizing medium exists and then add *N* ammonium thiocyanate solution. Copper precipitates as the dimeric cuprous thiocyanate, $Cu_2(SCN)_2$. Filter, wash with cold water. Collect the filtrate and the washings. Precipitate the cadmium in the filtrate with hydrogen sulfide and estimate in a manner similar to lead by comparing with standard cadmium sulfide precipitates in Nessler tubes. This method has a large error, at times, since cadmium sulfide is often contaminated with a basic salt in the hydrogen sulfide precipitation.

In the presence of copper, 1-(2-quinolyl)-4-allylthiosemicarbazide[28] may be used as a precipitant for cadmium. One ml. of a saturated 50 per cent alcohol solution of this reagent with 10 ml. of solution gives a precipitate with 1 part per million of cadium in the presence of potassium iodide. Zinc, nickel, cobalt, sulfate, and ammonia interfere. The metals may be eliminated by the usual sulfide separation, the sulfates with barium and the ammonia by evaporation.

A method for the determination of cadmium using dithizone is given by Sandell.[29,30] Other methods for the determination of cadmium with the aid of organic reagents such as anthranilic acid, quinaldinic acid, naphthoquinoline, and others are detailed by Prodinger.[30]

D. MANGANESE

Manganese poisoning due to manganese-bearing dusts and compounds is comparatively rare. However, serious and even fatal poisonings have occurred through its use in industry. Among its many and growing uses are the manufacture of manganese steels and alloys, its use in the prevention of blow-holes in castings, in the neutralization or decolorization of iron color in glass, as an aid in the liberation of chlorine, in the lacquer, paint, varnish, and enamel industry as a dryer, and as manganese dioxide in the so-called "dry" cell or battery. It is also a hazard where manganese ores are crushed. There is generally a manganese hazard in welding operations, since many welding rods contain manganese.

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[28] A. W. Scott and E. G. Adams, *J. Am. Chem. Soc., 57,* 2541 (1935).

[29] E. B. Sandell, *Ind. Eng. Chem., Anal. Ed., 11,* 364 (1939).

[30] W. Prodinger, *Organic Reagents Used in Quantitative Inorganic Analysis,* Elsevier, New York, 1940.

1. Physiological Response

Manganese causes systemic poisoning, attacks the neuromuscular system, and is not in the metal-fume fever group. The disease is characterized by muscular stiffness and incoordination, which progresses until disability results. It is usually first apparent as disturbances in gait and difficulty in stepping backward without falling down, speech disturbances including stuttering and running together of words, muscular twitchings or tremors, and occasionally a masked facial expression. There may be complaints of extreme drowsiness, weakness, or lassitude, muscular twitchings and cramps, and difficulty in walking and talking. Later, many other parts of the body may be affected and a crippling disability results. Longevity is not affected.

In a study of chronic manganese poisoning in an ore-crushing mill,[31] it was found that none of nine men exposed to less than 30 mg. of manganese per cubic meter had the disease, although only two of these nine had been employed for more than 3 years; on the other hand five of six men exposed for more than 3 years to atmospheric concentrations of manganese exceeding 90 mg. per cubic meter were found to have the disease. Tests made by these investigators in a modern mill showed that workers' exposure could be reduced to at most 6 mg. per cubic meter by the use of enclosed machinery, mechanical conveyors, and exhaust ventilation.

The maximum permissible concentration of manganese dust and fumes in the working atmosphere recommended by the American Standards Association[32] is 60 mg. per 10 cubic meters of air.

2. Determination

The dusts and fumes of materials containing manganese may be collected by the methods previously described for the collection of other dusts and fumes, the impinger and precipitator being more commonly used.

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[31] R. H. Flinn, P. A. Neal, W. H. Reinhart, J. M. DallaValle, and W. B. Fulton and A. E. Dooley. *U. S. Pub. Health Service, Bull. 247* (1940).

[32] *Am. Standards* Z37.6—1942.

a. Willard-Greathouse Periodate Method[33–35]

The periodate method is suitable for estimating quantities of manganese of less than 1 mg. After removal of chlorides, manganous salts are oxidized to permanganate by means of periodate and the color produced is compared with that of standards. Fairhall[36] prefers the periodate method to the persulfate method described below.

If necessary, ash the sample or a portion of it in a silica dish. Take up in hydrochloric acid and evaporate to dryness. Evaporate liquid samples to dryness with concentrated hydrochloric acid. Add a few ml. of sulfuric acid (1:2) and 3 to 4 drops of concentrated nitrate acid. Evaporate carefully to dryness on a water bath and sand bath, finishing the evaporation by gentle ignition with a Bunsen flame. Add 2 to 2.5 ml. of sulfuric acid (1:2) and a little water, and evaporate to white fumes of sulfur trioxide, thus removing all traces of chlorides. Cool, dilute, and filter into a 50-ml. flask for oxidation. Add to the solution one or two small pieces of pumice stone, previously purified by boiling with 5 per cent sulfuric acid, and a little periodate. Evaporate down to about 10 ml., when the concentration of sulfuric acid will be a 5–6 per cent solution.

Add 0.3 g. of sodium periodate or potassium periodate and insert a loosely fitting pear-shaped glass stopper or similar arrangement in the neck of the flask. Heat to boiling, immerse in a boiling water bath, and heat for 30 minutes. Cool and transfer to colorimeter tubes. Depending on the depth of color, use 10-, 22.5-, 50-, or 100-ml. tubes, and dilute to the mark accordingly. If diluted with water before matching, the solution should be boiled in the water bath for 15 minutes longer.

Preparation of Standard. Standard Manganous Sulfate.—Dissolve 0.1438 g. of potassium permanganate in water containing 2 to 3 ml. of 2 *N* sulfuric acid. Reduce by the addition of 0.4 g. of sodium bisulfite. Boil off the excess sulfur dioxide, cool, transfer to a 1-liter volumetric flask, and make to volume. One ml. is equivalent to 0.05 mg. of manganese.

Sulfuric Acid Reagent. Add 120 ml. of concentrated sulfuric acid to

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[33] H. H. Willard and L. H Greathouse, *J. Am. Chem. Soc., 39,* 2366 (1917).

[34] M. B. Richards, *Analyst, 55,* 554 (1930).

[35] *Standard Methods of Water Analysis (8th ed.),* Am. Pub. Health Assoc., New York, 1936.

[36] L. T. Fairhall, *U. S. Pub. Health Service, Bull. 247,* 31 (1940).

1,500 ml. of water. Dilute to 2 liters. Add 2.4 g. of sodium periodate (sodium paraperiodate, $Na_2H_3IO_6$), heat to boiling, and place in a boiling-water bath for 30 minutes. This gives a 6 per cent by volume solution of sulfuric acid.

Color Standard. Oxidize exactly 20 ml. of the standard manganous sulfate solution to which are added 1.2 ml. of concentrated sulfuric acid and 30 ml. of 6 per cent sulfuric acid, with 0.3 g. of periodate in the usual way. Cool, transfer to a 1-liter volumetric flask, and make up to volume with the 6 per cent sulfuric acid reagent to 1 liter. One ml. of this solution is equivalent to 0.001 mg. of manganese.

b. Persulfate Method[37-39]

In this method the manganous sulfate is oxidized to permanganate by means of ammonium persulfate (ammonium peroxydisulfate).

Samples containing much chloride and organic matter are best freed of chloride and the organic matter in the manner described under the periodate method. Samples containing little chloride or organic matter may be treated as follows. Take an aliquot containing not more than 0.2 mg. of manganese. Add 2 ml. of nitric acid and adjust to 50 ml. volume. Precipitate any chloride by the addition of silver nitrate solution, containing 20 g. of silver nitrate, $AgNO_3$, in 1 liter of water, and add at least 1 ml. in excess. Add about 0.5 g. of ammonium persulfate crystals and warm the solution until the maximum permanganate color is developed. This usually takes about 10 minutes. At the same time prepare standards by diluting portions of 0.2, 0.4, 0.6 ml., etc., of the standard manganous sulfate solution to about 50 ml., and treat them exactly as the sample was treated. Transfer the sample and the standards to 50-ml. Nessler tubes and compare the colors immediately.

To prepare the standard manganous sulfate solution for this method, dissolve 0.2873 g. of potassium permanganate in about 100 ml. of distilled water. Acidify the solution with sulfuric acid and heat to boiling. Add slowly a sufficient quantity of dilute solution of oxalic acid to discharge the color. Cool and dilute to 1 liter. One ml. of this solution contains 0.1 mg. of manganese.

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[37] *Standard Methods of Water Analysis* (8th ed.), Am. Pub. Health Assoc., New York. 1936.

[38] H. Marshall, *Chem. News, 83,* 76 (1901).

[39] D. H. Wester, *Rec. trav. chim., 39,* 414 (1920).

E. SELENIUM

One of the major uses of selenium compounds is in the glass industry, where they are used to color glass a deep red and to neutralize iron color. The use of selenium in industry is growing. Among these new uses may be mentioned red and yellow glazes; paint and ink pigments; production and coloring of plastics; alloying of machinable stainless steels; alloying of free-machining copper-base alloys; rubber accelerators and antioxidants; fireproofing of electric cable; photoelectric cells and apparatus; and in chemicals.[40] Danger of exposure to selenium is not limited to those industries where it or its compounds are used as a raw material, for it is also a hazard where it occurs as an impurity or contaminant, as in the manufacture of chamber sulfuric acid from seleniferous iron pyrites or in the electrolytic refining of copper where selenium is to be found in the anode sludge.

TABLE 11

Industries and Their Possible Selenium Hazards[40]

Industry	Source of hazard	Type of hazard
Primary industries:		
Copper	Ore concentrate and flue dusts, sludges	Se, SeO_2 and mixed dusts
Lead and zinc	"	"
Pyrites roasting	Roasting towers, sludges	Mixed dusts, Se
Lime and cement (certain areas)	Dust, kiln gases	Mixed dusts, SeO_2
Secondary industries:		
Glass, ceramics	Melting pots and furnaces	Fumes of Se, SeO_2
Rubber	Vulcanizing and curing processes	Organic vapors, H_2Se
Steel and brass	Alloy furnaces	Dusts, Se, SeO_2. Fumes
Paint and ink pigments	Pigment compounding and mixing	H_2Se, SeO_2, soluble dusts
Plastics	Mixers, presses	Organic vapors
Photoelectric	Melting and casting operations	Vapors, Se, SeO_2
Chemicals	Mixing, melts, synthesis	Se, SeO_2, H_2Se, organic vapors

1. Physiological Response and Toxicity

Selenium is closely allied to sulfur and tellurium in its chemical properties. It follows arsenic in the periodic system of the elements and also resembles that element in some of its chemical and physical properties. One marked characteristic that they have in common is that they are both semimetallic. In its physiological action on the human system, it also resembles arsenic. It forms a poisonous compound with hydrogen, hydrogen selenide, which is a colorless, inflammable gas with an intensely offensive odor similar to that of rotten horse-radish. The subject of selenium-bearing soils has been given a great deal of study by the U. S. Bureau of Chemistry and Soils.[41] It has been shown that 4 ppm. is an outside tolerance limit in foodstuffs, and that 3 ppm. is a safer tolerance.[42] There can be little question that seleniferous materials are poisonous.

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[40] H. C. Dudley, *U. S. Pub. Health Service, Reprint 1910* (1938).

The acute effects of ingestion of soluble selenium compounds may be summarized as consisting of progressive anemia, loss of weight, abdominal pains, early cellular destruction in the liver, with later pathological changes throughout the organism. The ingestion of small quantities of selenium compounds over a long period results in retrograde changes in the liver and kidneys, accompanied by general debility. The acute and subacute effects resulting from single exposures of guinea pigs to hydrogen selenide are, primarily, an early severe fatty metamorphosis of the liver and late hypertrophy of the spleen.

The symptoms of men poisoned by selenium while employed at copper refineries extracting or purifying selenium are given by Hamilton[43] and Dudley[44] as pallor, gastrointestinal disturbances, garlicky odor of breath and perspiration, irritation of nose and throat (rose cold), coating of tongue, metallic taste in mouth, and nervousness. The excretion of selenium in the urine is conclusive evidence that workers are absorbing selenium.

The recommended maximum allowable concentration for selenium compounds, calculated as selenium, is 0.1 mg. per cubic meter of air.

Dudley and Miller[45] found that guinea pigs exposed to 0.57 mg. of hydrogen selenide per liter of air for 10 minutes died within 5 days; 93 per cent of the animals exposed to 0.043 mg. per liter for 30 minutes died within 30 days; and all animals exposed to 0.02 mg. per liter for 60 minutes died within 25 days. Thus, this substance is extremely toxic. Fairhall[46] states that the maximum allowable concentration of hydrogen selenide should be lower than that which produces irritation. A concentration of 1.5 ppm. is intolerable to man. The recommended maximum allowable concentration is 0.1 ppm.

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[41] H. G. Byers, *U. S. Dept. Agr., Tech. Bull. 530* (1936).

[42] H. E. Munsell, G. M. DeVaney, and M. H. Kennedy, *U. S. Dept. Agr., Tech. Bull 534* (1936).

[43] A. Hamilton, *Industrial Toxicology*, Harper, New York, 1934.

[44] H. C. Dudley, *Am. J. Hyg., 23*, 181 (1936).

[45] H. C. Dudley and J. W. Miller, *U. S. Pub Health Service, Reprint* 1855 (1937)

[46] L. T. Fairhall, *Ind. Hyg. Newsletter, 7*, No. 3, 9 (1947).

Selenium oxychloride, $SeOCl_2$, is toxic and extremely vesicant. As little as 0.01 ml. applied to the skin of rabbits will cause death within 24 hours[47] The toxic action of this compound is in part attributable to the selenium absorbed, as evidenced by the presence of the element in the blood and liver of animals treated in this way.

Selenium oxychloride produces third-degree burns when applied to the skin of man. The burn is painful and slow to heal. If selenium oxychloride, which is a strong chlorinating and oxidizing agent, is used, it is best to have large quantities of water available for immediate use, for rapid flushing with water will hydrolyze it and thus prevent burns.

2. *Sampling*[48,49]

Vapors and gaseous components of plant atmospheres and contaminations in laboratory workrooms may be sampled quantitatively by means of the apparatus outlined in Figure 84. The sampling arrangement for absorbing gases or vapors consists first of a sintered-glass plate, overlaid by a fine, dried asbestos mat *A*, which is designed to screen out all solid particles or droplets that might enter the bubblers. After passing this screen the air-gas mixture is bubbled successively through two bubblers

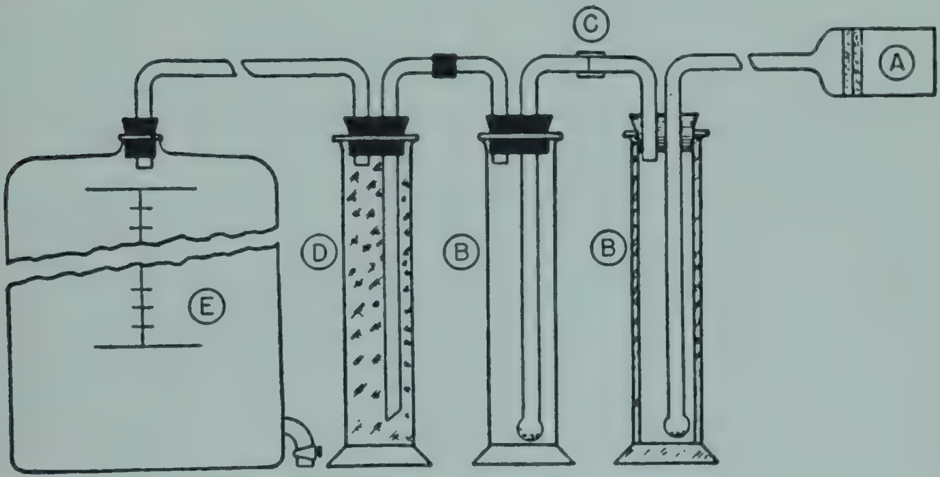

Fig. 84. Selenium sampling apparatus.[49]

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[47] H. C. Dudley, *U. S. Pub. Health Service, Reprint 1901* (1938).

[48] H. C. Dudley, *Am. J. Hyg., 24,* 227 (1936).

[49] H. C. Dudley, *U. S. Pub. Health Service, Reprint 1910* (1938).

B, each containing a mixture of 50 ml. of 40–48 per cent hydrobromic acid, with free bromine 10 per cent by weight. The oxidizing power of this solution is utilized to oxidize the selenium, so that it can be dissolved by the acid medium. After passing through the bubblers, the air stream moves into an absorption tube *D* containing some suitable material, such as coarse granular soda lime or activated charcoal or calcium hydroxide, to remove hydrogen bromide and bromine vapors. The aspirator bottle *E* contains water. As this water issues from the outlet at the bottom of the bottle, air is drawn into the bottle through the bubbler train. Since the volume of water displaced by the air can be read, it is possible to ascertain the amount of selenium contained in this volume of air by an analysis of the bubbler solutions. A sample of 10 liters will prove sufficient in gas-air mixtures with selenium concentrations of more than 0.01 mg. of selenium per liter. For smaller concentrations, 20 liters or more of the atmosphere must be sampled. Two bubblers have been found sufficient to trap all the selenium in atmospheres with concentrations ranging from 0.005 to 0.30 mg. of selenium per liter. The maximum rate of sampling used with uniform success was 2 liters per minute.

The aspirator bottle should be of sufficient capacity so that water to the height of 5 to 8 inches remains in the bottle after 10 or 20 liters have been withdrawn. This layer of water is necessary to overcome the resistance of the bubbler train caused by the hydrostatic pressure of the hydrobromic acid in the bubblers. By controlling the rate of outflow of the water from the sampling bottle by means of the outlet stopcock, it is possible to obtain a relatively constant sampling rate. With decrease in the height of the water in the sampling bottle, the rate of sampling tends to decrease. Suitable manipulation will overcome this difficulty.

For trapping selenium-bearing dusts, the paper-thimble method described in Chapter V may be used. The filter shown in Figure 84 is also suitable for certain dusts. This filter consists of a tube in which is sealed a sintered-glass plate, approximately 1.5 inches in diameter. This porous plate is overlaid by a smooth, fine, dried asbestos mat. The mat may be easily washed off and reformed from prepared Gooch asbestos suspensions. By drying the mat at 105° C. for 1 hour, very little resistance will be built up in the suction lines. Such a mat will screen out the more commonly encountered dust as well as fog particles.

The filter, prepared as above, may be acid-washed, dried, and weighed. The dusty air may be drawn through the filter, which is again dried and weighed. The weight of dust particles per unit volume of air may be calculated if the volume of air sampled is known.

Fumes of selenium compounds and also selenium-bearing dusts may be sampled with the aid of an electrostatic precipitator.

3. Determination[50,51]

Combine the contents of the bubblers and precipitate the selenium directly with sulfur dioxide or solid sodium sulfite. After the bromine is completely discharged, add 1 or 2 g. of solid hydroxylamine hydrochloride. Heat the mixture on a steam bath for 30 minutes and allow to settle over night. Filter the resulting precipitate on asbestos, redissolve with 40 per cent hydrobromic acid containing 0.5 per cent of free bromine, and reprecipitate as above, using filtered, saturated aqueous solutions of the reagents. If sufficient selenium is present, the second precipitate may be weighed on a tared Gooch crucible, after drying 1 hour at 105° C.

If the total amount of selenium in the combined hydrobromic acid bubbler solutions is less than 1 mg., partially remove the free bromine with solid sodium sulfite. Sufficient bromine should remain to impart a deep yellow color to the solution. Then proceed with the distillation method as described on page 272, estimating the selenium colorimetrically.[52,53]

If the total amount of selenium in the bubbler solutions ranges between 1 and 5 mg., it may be made up to standard volume of 100 ml. on dissolving the first precipitate with hydrobromic acid and bromine. A suitable aliquot may be taken and made up to 25 ml., the colorimetric estimation being carried out with this fraction. In practice the colorimetric estimation has been found to be most accurate when the amount of selenium is between 0.05 and 0.50 mg. of selenium per 25 ml. of the sample solution. The concentration of hydrogen bromide must be kept between 25 and 30 per cent, since at this acid concentration the precipitate appears with readiness and in a form most easily matched in color. Hydrobromic acid of 25 to 30 per cent concentration has been found to be most advantageous for the precipitation of selenium from hydrobromic acid solutions. As a rough approximation, when precipitating selenium from 48 per cent hydrobromic acid solutions, add aqueous solutions of reagents or water to increase the volume one-third to obtain the 25 to 30 per cent mixture.

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[50] H. C. Dudley, *U. S. Pub. Health Service, Reprint 1910* (1938).

[51] H. C. Dudley, *Am. J. Hyg., 24,* 227 (1936).

[52] H. C. Dudley and H. G. Byers, *Ind. Eng. Chem., Anal. Ed., 7,* 3 (1934).

[53] H. C. Dudley, *Am. J. Hyg., 23,* 169 (1936).

In practice, the above method for the absorption of gaseous selenium products has been found applicable to a variety of gases, namely, hydrogen selenide, selenium dioxide, ethyl selenide, and methyl selenide, as well as various mixtures of unknown volatile selenium compounds produced on putrefaction of organic materials.[54]

Distillation Method.[55] The following method is based on the fact that selenium may be separated from all other elements except arsenic and germanium by distillation with concentrated hydrobromic acid. The selenium must be in, or converted into, the sexavalent condition before distillation in order to insure its distillation with the acid will be complete. In most cases the conversion may be accomplished by the use of bromine. The excess bromine distills at a low temperature and the hydrobromic acid then reduces the selenium to the quadrivalent condition. In this form it readily distills along with the hydrobromic acid. The selenium is subsequently estimated in the distillate by reduction with hydroxylamine hydrochloride and sulfur dioxide.

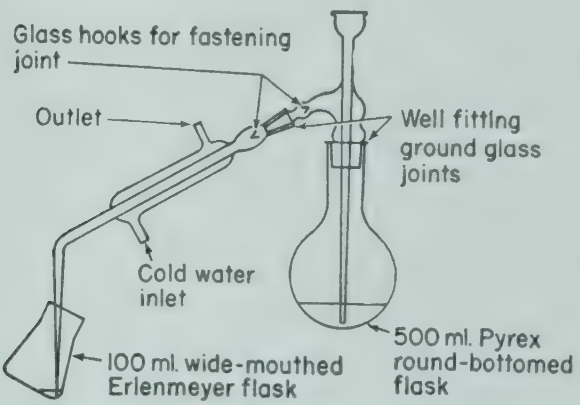
Glass hooks for fastening joint
Outlet
Well fitting ground glass joints
Cold water inlet
500 ml. Pyrex round-bottomed flask
100 ml. wide-mouthed Erlenmeyer flask

Fig. 85. Selenium distillation apparatus.[55]

Transfer the hydrobromic acid-bromine mixture from the bubblers to the distillation apparatus (Fig. 85). Triturate the seleniferous dust with 100 ml. of concentrated hydrobromic acid and transfer to the distillation apparatus. The apparatus consists of a Pyrex, 500-ml. round-bottom flask fitted with a ground-stopper into which has been sealed a thistle tube with a stem long enough to reach within 5 mm. of the bottom of the flask. The ground-glass stopper also has a side arm with a ground-glass end fitted to a condenser whose end is drawn out into a long adapter, bent and with a capillary tip so that it may fit easily into a 100-ml. wide-mouth flask, which acts as the receiver.

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[54] H. C. Dudley, *U. S. Pub. Health Service, Reprint 1910* (1938).

[55] W. O. Robinson, H. C. Dudley, K. T. Williams, and H. G. Gyers, *Ind. Eng. Chem., Anal. Ed., 6,* 274 (1934).

Connect the distillation apparatus described with the adapter just below the surface of 2 to 3 ml. of bromine water in the receiver flask and apply heat gradually. One or 2 g. of bromine should distill over in the first few milliliters of distillate. If insufficient bromine has been added to produce this quantity of bromine, more must be added through the thistle tube. A somewhat greater excess of bromine does no harm, but too great an excess is to be avoided because of the formation of too much sulfuric acid later. Collect 30 to 50 ml. of the distillate by increasing the heat. Make a second or even third distillation, with intervening additions of hydrobromic acid and bromine through the thistle tube, unless it is certain from experience that all the selenium is in the first distillate. Remove the distillate and pass in sulfur dioxide until the yellow color due to bromine is discharged. Add 0.25 to 0.5 g. of hydroxylamine hydrochloride, stopper the flask loosely, put it on the steam bath for 1 hour, and allow to stand overnight at room temperature. If selenium is present, it will appear as a characteristic pink or red precipitate. If much selenium is present, it will shortly turn black.

Collect the precipitated selenium on an asbestos mat in a Gooch crucible, and wash slightly with hydrobromic acid containing a little hydroxylamine hydrochloride. Dissolve the selenium on the pad by passing through 10 to 15 ml. of a solution of 1 ml. of bromine in 10 ml. of hydrobromic acid in small quantities and wash into a 25-ml. measuring flask if the quantity is small and is to be estimated colorimetrically. If it is over 0.5 mg., filter into a small beaker, precipitate as before, gather on an asbestos mat as before, and wash with hydrobromic acid containing a little hydroxylamine hydrochloride and then with water. Prepare a tare in the same way. Dry at 90° C. for 1 hour, place in a vacuum desiccator, and exhaust the air while the crucibles are still hot. Cool for $^1/_2$ hour. Allow air to enter the desiccator, cool an additional $^1/_2$ hour, and weigh against the tare. Check the weight by drying again.

Colorimetric Estimation. If the quantity is small and is to be estimated colorimetrically, add 1 ml. of a solution containing 5 per cent gum arabic and precipitate the selenium by sulfur dioxide and hydroxylamine hydrochloride. Prepare comparison solutions containing known quantities of selenium in exactly the same manner and allow them to stand overnight. Shake the standards and test solution and compare the depth of color in Nessler tubes. This comparison is best carried out in sunlight. It is difficult to match solutions containing more than 0.5 mg. of selenium in 25 ml. The color comparison is most satisfactory when 0.01 to 0.1 mg. is present.

As a variation of the above method colorimetric method, the following procedure may be employed for the determination of selenium dioxide in air. Trap the air by passing it through an absorber containing 25 ml. of water. Transfer the solution to a 50-ml. volumetric flask. Add sufficient hydrochloric acid, sp. gr. 1.19, to make the acidity equal to 1:4, and complete to volume. Transfer a known aliquot, 20 to 25 ml. to a Nessler tube, add 1 ml. of a 5 per cent solution of gum arabic or gum ghatti solution and 1 ml. of 10 per cent stannous chloride solution, and estimate the amount of selenium dioxide by comparison with standard solutions treated similarly.[55a]

Titrimetric Method. Transfer the liquid from the absorber to a flask, add approximately 0.1 g. of sodium bicarbonate, 1 ml. of starch solution, and 0.0025 *N* iodine solution from a burette until a blue color is obtained. Decolorize the solution with 1–2 drops of 0.0025 *N* sodium thiosulfate solution. Add 6–10 ml. of 0.0025 *N* sodium thiosulfate solution, acidify the mixture with 10 ml. of sulfuric acid (1:5), shake and titrate immediately with 0.0025 *N* iodine solution. Determine the amount of selenium dioxide from the difference between the number of milliliters of iodine solution required for the thiosulfate and that required for the titration. One ml. of 0.0025 *N* iodine solution is equivalent to 0.0695 mg. of selenium dioxide.

4. *Hydrogen Selenide*

A soda lime tube may be used with success in sampling atmospheres for hydrogen selenide content. The tube is of simple construction, being made from a 6- by $^3/_4$-inch Pyrex test tube by sealing a glass tube in the closed end. At sampling rates of 4 liters per minute or less, these tubes, when charged with fresh, dry soda lime, are satisfactory at all concentrations below 0.10 mg. of selenium per liter of air. The selenium is recovered from the soda lime tube by distillation with hydrobromic acid as described. The selenium so distilled may be weighed or estimated colorimetrically.

[55a] M. E. Chernyi, *Trudy i Materialy Sverdlov. Inst. Eksptl. Med.*, 1940, No. 4, 175; *Khim. Referat. Zhur.*, *4*, No. 5, 67 (1941); *Chem. Abstracts*, *37*, 5935 (1943).

F. TELLURIUM

Tellurium is related chemically to selenium and sulfur but it resembles arsenic in its physiological action. Its principal use in industry is in the coloring of glass, in rubber compounding, in stainless steel, and in chilled iron. However, it may be a hazard wherever tellurium-bearing ores are worked, as in the electrolytic refining of lead.[56] Hydrogen telluride is a hemolytic agent. The most pronounced physiological effects of the inhalation of tellurium-bearing fumes and dusts are dry mouth, metallic taste, inhibition of sweat, languor, somnolence, loss of appetite, salivation, nausea, vomiting, garlic odor of the breath, and constipation.

The recommended maximum allowable workroom concentration for tellurium fumes[57] is less than 0.1 to 1 mg. per 10 cubic meters. The accepted value is the latter.

Detection and Determination

Tellurium compounds can be trapped in water or in hydrochloric acid. If water is used add hydrochloric acid and then pass in sulfur dioxide gas. Tellurium is precipitated. Selenium will also precipitate, as previously described, but may be separated from tellurium by the distillation method given on page 272.

If sufficient tellurium is present it may be estimated gravimetrically by precipitation with sulfur dioxide and hydrazine sulfate.

Prepare the test solution so that it is about 3 N with respect to hydrochloric acid, that is, 1:3. Heat to boiling; add 15 ml. of a saturated solution of sulfur dioxide; 10 ml. of a 15 per cent solution of hydrazine hydrochloride or sulfate; and then 25 ml. more of saturated sulfur dioxide solution. Boil till the precipitate settles, which takes about 5 minutes. Filter through a tared, prepared Gooch crucible. Wash quickly with hot water till free of chlorides, then with alcohol, and dry in a thermostatically controlled oven at 105° C.

Tellurium in the form of tellurates or telluric acid may be estimated titrimetrically by boiling with hydrochloric acid. Chlorine is evolved as shown by the following formula:

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[56] M. D. Shie and F. E. Deeds, *U. S. Pub. Health Repts.*, *35*, 939 (1920).

[57] H. H. Steinberg, S. C. Massari, A. C. Miner, and R. Rink, *J. Ind. Hyg. Toxicol.*, *24*, 183 (1942).

$$K_2TeO_4 + 4HCl \longrightarrow 2KCl + H_2TeO_3 + H_2O + Cl_2$$

The chlorine is trapped in an efficient bubbler containing potassium iodide solution. The liberated iodine is then titrated with 0.1 *N* or other appropriate standard sodium thiosulfate solution. One ml. of 0.1 *N* thiosulfate solution is equivalent to 0.006375 g. of tellurium.

Methods of analysis for tellurium are also discussed by Steinberg[57] and co-workers.

G. VANADIUM

Exposure to vanadium occurs principally in three fields: the working of its ores; the manufacture of vanadium steels; and as a mordant in dyeing. Fairhall[58] states that there is no question that vanadium compounds are toxic, for even such materials as the crude ore dust cause striking toxic effects.

The principal early symptoms produced by vanadium poisoning are anemia, coughing, emaciation, irritation of the mucous membranes, and gastrointestinal disturbances.[59] Later symptoms include nervous disorders and vertigo. Lung damage, pneumoconiosis, and systemic intoxication have been shown to result from vanadium poisoning.

In a study of vanadium poisoning in rats[60] it was found that there was no apparent cumulative effect but that there was an immediate nervous reaction.

Detection and Determination

Vanadium fumes and dusts may be trapped in nitric or sulfuric acids, since most vanadium minerals yield readily to acid treatment.

Vanadium, freed from molybdenum, titanium, cerium, and other interfering metals, may be detected by the use of hydrogen peroxide, with the production of a red brown color. Dilute the sulfuric acid solution so that it is about 1:4. Transfer to a volumetric flask. Add 1 to 2 ml. of 30 per cent hydrogen peroxide. Make to volume with sulfuric acid (1:4) and compare with standards similarly treated. The colorimetric peroxide method is used mainly for the detection and confirmation of the presence of vanadium.

Vanadium may be estimated by preliminary reduction to the quadrivalent state with sulfur dioxide; expulsion of the sulfur dioxide with carbon dioxide; and subsequent titration with hot standard potassium permanganate solution.

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[58] L. T. Fairhall, *Ind. Hyg. Newsletter, 7*, No. 1, 6 (1947).

[59] F. P. Underhill, *Toxicology*, Blakiston, Philadelphia, 1928.

[60] E. P. Danial and R. D. Lillie, *U. S. Pub. Health Repts.*, *53*, 765 (1938).

If nitric acid was used to trap the sample, evaporate to dryness. Take up again in sulfuric acid. Evaporate carefully at a low temperature to sulfur trioxide fumes. Do not fume for longer than 10 minutes. There is no loss of vanadium even when baked at 175° C. or when heated at this temperature with sulfuric acid.[61]

Dilute the solution so that there are about 2 parts of acid to 98 of water. Heat to boiling and add concentrated potassium permanganate solution till the mixture is pink. Reduce the vanadium by passing in sulfur dioxide gas, preferably from a cylinder of the gas, for 5–10 minutes. Pass in carbon dioxide gas free from oxygen and hydrogen sulfide to free the reaction mixture from sulfur dioxide. This may be tested by passing the exuent gas through very dilute potassium permanganate solution. Cool the mixture to 60–80° C. and titrate with standard 0.1 N potassium permanganate solution. One ml. of 0.1 N potassium permanganate solution is equivalent to 0.0051 g. of vanadium.

For the separation of vanadium from other interfering metals, consult one of the texts on inorganic analysis listed in the reference at the end of the chapter.

H. THALLIUM

Industrial exposure to thallium occurs in the manufacture of thallium compounds to be used in rat and vermin poisons, luminous paint, window glass, and in some industries where it is a contaminant, as in the flue dust of sulfuric acid works. Thallium compounds have been used unwisely as depilatories. It resembles lead in its toxic properties and is a cumulative poison. The principal symptoms exhibited in thallium poisoning are loss of hair, cramps, pains in the limbs with paralysis, diarrhea, nephritis, cardiac degeneration, and death.

Detection and Determination

Thallium may be detected spectroscopically by the green color it gives to the flame. It can be precipitated from sodium carbonate solution, in the presence of potassium cyanide, by ammonium sulfide. The precipitated thallous sulfide is soluble in hot 10 per cent sulfuric acid and may be reprecipitated as the chloride (thallous chloride, TlCl), as thallous iodide in solutions neutralized with sodium carbonate, and as thallous chromate, Tl_2CrO_4, from neutral solutions.

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[61] W. F. Hillebrand and G. E. F. Lundell. *Applied Inorganic Analysis*. Wiley. New York, 1929.

Small amounts of thallium may be estimated by a method similar to that used for copper by the liberation of iodine from thallic chloride, $TlCl_3$, by the addition of potassium iodide with the formation of thallous iodide, TlI, and free iodine which is subsequently titrated by standard sodium thiosulfate solution. A variation depending on an ether extraction is detailed below.

Thallium may also be estimated titrimetrically by oxidation from the thallous to the thallic state in hydrochloric acid solution by the use of standard potassium permanganate or bromate.[62,63]

Extraction-Titration Method.[64,65] Destroy organic matter with concentrated hydrochloric acid and potassium chlorate, or with 4 *N* hydrochloric acid and potassium chlorate, using 0.1 *N* potassium permanganate solution as a catalyst, or with nitric and sulfuric acids in the usual manner. In the latter instance it is necessary to add some free chlorine as, for instance, by use of a heated solution of potassium chlorate in 4 *N* hydrochloric acid.

Transfer the sample containing free chlorine to a Jacobs-Singer separatory flask. Check the reaction with starch-iodide paper. Add an equal volume of ether. Shake vigorously, allow the layers to separate, and draw off the ether layer into a separatory funnel. Add 1 to 2 ml. of sulfur dioxide water to the ether layer and shake vigorously, until the aqueous layer no longer reacts with starch-iodide paper. Adjust the volume of the aqueous layer to about 5 ml. and draw off into an evaporating dish. Shake out the ether layer with 2 ml. of water and add this washing to the evaporating dish. Repeat the extraction of the sample an additional two times with ether. Extract the second and third ether extractions successively with sulfur dioxide water and water. Add each aqueous extract and wash to the evaporating dish, making a total of six additions.

Evaporate the combined aqueous sulfur dioxide extracts on a steam bath in a hood. Transfer, with the aid of a glass rod and a few drops of nitric acid, to a 50- by 18-mm. Pyrex glass tube, add 0.2 ml. of concentrated sulfuric acid, and digest in the customary manner. Wash

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[62] H. Marshall, *J. Soc. Chem. Ind., 19,* 994 (1900).
[63] E. Zintl and G. Rienaecker, *Z. anorg. Chem., 153,* 276 (1926).
[64] A. A. Noyes, W. C. Bray, and E. B. Spear, *J. Am. Chem. Soc., 30,* 516, 559 (1908).
[65] J. F. Reith and K. W. Gerritsma, *Rec. trav. chim., 65,* 770 (1946).

the evaporating dish with drops of nitric acid, adding the washings to the digestion tube. The digestion may be considered complete when the sulfuric acid remains colorless or a light yellow.

Add 0.8 ml. of water, mix, cool, and filter with suction through a micro filter of sintered glass into a precipitation tube 40 x 10 mm. Adjust the volume to 1.8 ml., add 0.1 ml. of a freshly prepared saturated solution of sodium sulfite, $Na_2SO_3.7H_2O$, and mix with a glass rod. Add 0.2 ml. of 10 per cent potassium iodide solution and mix. An orange-yellow precipitate indicates thallium. Rinse off the rod and allow the covered tube to stand for 12 to 18 hours in the dark. Centrifuge at 1,500 r. p. m. for 5 minutes, pour off the supernatant liquid with the aid of a glass rod, and wash the precipitate with 2 ml. of 50 per cent alcohol, stirring the precipitate with the rod, which is rinsed off with a few drops of alcohol. Centrifuge and decant. Wash again with 2 ml. of 90 per cent alcohol.. At this point the precipitate may be estimated gravimetrically by the usual micro gravimetric methods, the factor Tl/TlI being 0.6160.

Titrimetric Procedure. Dry the tube. In the range of 10 to 250 micrograms of thallium add 0.1 ml. of glacial acetic acid and a small drop of bromine. Shake for a moment every 5 minutes until no solid particles are visible and allow to stand an additional 15 minutes. Transfer the contents of the tube to a 25-ml. flask with not more than 2 ml. of water. Heat until the mixture is light yellow, allow to cool, add 2 *M* sodium formate solution, prepared by dissolving 24.2 g. of sodium formate, $HCOONa.3H_2O$, in water and diluting to 100 ml., until the solution is colorless, and then add an excess of 0.2 ml. Mix carefully and moisten the walls of the flask. Allow to stand 5 minutes. Add 2 ml. of 30 per cent sodium chloride solution, 1 drop of 10 per cent potassium iodide solution, 0.2 ml. of 4 *N* sulfuric acid, and 5 drops of 0.2 per cent starch-indicator solution. Titrate with 0.01 *N* sodium thiosulfate solution.

Comparison solutions of thallium must be standardized because many salts are of dubious purity. Dissolve 131 mg. of thallous carbonate, Tl_2CO_3, or an equivalent amount of another salt in water and dilute to 100 ml. This is approximately 1 mg. of thallium per ml. Transfer 1 ml. of this solution to a 100-ml. flask, add 10 ml. of water, 0.3 ml. of glacial acetic acid, and sufficient bromine water to give a yellow color and 2 drops in excess. Allow to stand for 15 minutes, and remove the excess bromine with 2 *M* sodium formate solution. Allow to stand an additional 5 minutes, add 20 ml. of 30 per cent sodium chloride solution, 0.5 ml. of 10 per cent potassium iodide solution, 1 ml. of 4 *N* sulfuric acid solution, 2 ml. of 0.2 per cent starch-indicator solution, and titrate with 0.01 N sodium thiosulfate solution. One ml. of the latter is equivalent to 1.022 mg. of thallium.

Lead, mercury, copper, arsenic, antimony, bismuth, and iron do not interfere in this method.

I. ZINC

Zinc is not a poison in the usual sense of the word. That is to say, pure zinc, in contrast to metals such as lead, arsenic, antimony, and carmium, has virtually no poisonous qualities even if ingested in relatively large amounts. However, there are indications[66] that continuous ingestion of soluble zinc compounds, as in the instance of swallowing zinc-bearing dusts with the saliva, may cause chronic gastritis with emesis. Certain zinc compounds are caustic. The one most commonly met in industry is, as was mentioned, zinc chloride. This is used as a flux in soldering, and if spattered may cause bad burns. Zinc sulfate is also caustic, while zinc chromate may cause dermatitis. Other zinc compounds are harmful because of their state of subdivision. This is the greatest single hazard to workers in zinc and zinc products.

1. Metal-Fume Fever

It was formerly thought that zinc metal was the cause of brass-founders' ague, spelter shakes, and brass chills. The term metal-fume fever is now used to cover such affections.[67] It has been shown that the chill and fever thought to be produced by zinc oxide alone can also occur when oxides of other metals or finely divided powders of other metals are inhaled. Thus it has been demonstrated that zinc stearate, copper oxide,[68,69] and magnesium oxide can also give rise to this type of illness. Koelsch[70] concluded that metal-fume fever may occur from the inhalation of all heavy metals. Drinker[69,71] and his co-workers found that 45 mg. of zinc oxide, measured as zinc, per cubic meter of air could be inhaled for 20 minutes without causing symptoms. They found that in a metallurgical plant, 14 mg. per cubic meter produced no reaction in 8 hours.

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[66] D. M. Hegsted, J. M. McKibben, and C. K. Drinker, *U. S. Pub. Health Repts., Supplement 179* (1945).

[67] A. Hamilton, *Industrial Toxicology,* Harper, New York, 1934.

[68] C. C. Sturgis, P. Drinker, and R. M. Thompson, *J. Ind. Hyg., 9,* 88 (1927).

[69] P. Drinker, R. M. Thomson, and J. L. Finn, *J. Ind. Hyg., 9,* 98, 187, 331 (1927).

[70] F. Koelsch, *J. Ind. Hyg., 5,* 87 (1923–24).

[71] C. K. Drinker and L. T. Fairhall, *U. S. Pub. Health Repts., 48,* 955 (1933).

The recommended maximum allowable concentration for zinc oxide fumes is 15 mg. per cubic meter of air.

2. *Sampling*

Zinc-bearing dust-laden air may be sampled by means of the Greenburg-Smith impinger, as described for the sampling of lead dust. Otherwise the fumes may be flocculated in an electrical precipitator. An alternative method is to pass air through a trap containing cotton moistened with nitric acid.

Evaporate, dry, and char the sample or an aliquot. Then ash in an electric muffle oven at 450° C. or low red heat. Extract the ash with hydrochloric acid (1:1). Filter. If a clean ash has not been obtained, it may be necessary to re-ash the filter paper and residue in the original dish and then re-extract with hydrochloric acid (1:1).

3. *Determination*

a. Ferrocyanide Method[72,73]

Small quantities of zinc may be estimated by the use of the ferrocyanide method. The zinc is freed from iron by the use of cupferron or phosphate. It is precipitated as the sulfide with the addition of copper, if necessary, to act as a collector. The sulfides are redissolved and the zinc is separated from the copper by the usual sulfide separation. Zinc is then converted to the chloride and estimated with ferrocyanide, either by titration using uranium acetate as an external indicator, or nephelometrically.

Preparation of Reagents. Potassium Ferrocyanide Solution. Dissolve 3.464 g. of recrystallized potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, in water and dilute to 1 liter. Allow to stand for a day or two and filter from any residue. This solution may be standardized by running a titration against known amounts of standardized zinc chloride solution as described in the method. One ml. of this solution is equivalent to 1 mg. of zinc.

Standard Zinc Chloride Solution.—Dissolve 1.2446 g. of ignited zinc oxide in a slight excess of hydrochloric acid (1:1). Dilute to 1 liter with water. One ml. is equivalent to 1 mg. of zinc.

Uranium Acetate Solution.—Dissolve 40 g. of uranium acetate [uranyl acetate, $UO_2(C_2H_3O_2)_2.2H_2O$] in 800–900 ml. of water. Allow to stand

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[72] L. T. Fairhall, *J. Ind. Hyg.*, *8*, 165 (1926).
[73] K. R. Drinker, J. W. Fehnel, and M. Marsh, *J. Biol. Chem.*, *72*, 375 (1927).

for several days. Filter from any residue into a volumetric flask and dilute to 1 liter.

Procedure. Adjust the volume of the prepared hydrochloric acid solution of zinc to about 75 ml. containing 10 to 15 ml. of hydrochloric acid (1:1). To precipitate iron, add to the cold solution an excess of an aqueous solution of cupferron (ammonium nitrosophenylhydroxylamine). The iron is completely precipitated when white crystals of the cupferron are noticed on further addition of the reagent. If a colloid forms, shake and stir until it is flocculated. Filter. Partly neutralize with sodium hydroxide solution and add ammonium acetate until the free hydrochloric acid is replaced by acetic acid, as is shown by using methyl orange as indicator. Add 0.5 mg. of copper as copper nitrate to act as a collector and saturate with hydrogen sulfide. Filter. Wash the precipitate with water and finally with hot alcohol. Dissolve the precipitate from the filter with alternate washings of concentrated nitric acid and hot water, catching the filtrate in the original sulfide precipitation vessel, until completely dissolved. Evaporate to dryness. Add 1 ml. of sulfuric acid (1:2) and 2 ml. of nitric acid. Heat in a hood until all traces of organic material have been oxidized and the excess sulfuric acid has been driven off. Dissolve the residue in 5 ml. of hydrochloric acid (1:1) and 20 ml. of water. Heat to boiling and titrate with the standard potassium ferrocyanide solution, using a spot plate and uranium acetate as an external indicator.

Nephelometric Method.[74-77] As an alternative method the following may be used. Iron is not precipitated but is held in solution by sodium citrate. The mixed sulfides of copper and zinc are precipitated as before but the ionic strength of the salts in the final solution is adjusted so that the sensitivity of the reaction with ferrocyanide is increased.

Adjust the volume of the prepared hydrochloric acid solution of the zinc to about 75 ml., add 5 g. of sodium citrate, 2 mg. of copper as copper sulfate, and a drop of thymol blue indicator. Add dilute potassium hydroxide solution until the solution becomes yellow and then add a drop of bromophenol blue. If the solution is bluish at this point, add dilute acid until the yellow color is just restored. Saturate the cold solution with hydrogen sulfide, filter and wash well to free from iron salts. Dissolve the combined sulfides in nitric acid and hydrochloric acid, dissolve the residue in hydrochloric acid, and adjust the pH of the solution

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[74] L. T. Fairhall and J. R. Richardson, *J. Am. Chem. Soc.*, *52*, 938 (1930).

[75] E. Bartow and O. M. Weigle, *Ind. Eng. Chem.*, *24*, 463 (1932).

[76] *Standard Methods of Water Analysis* (8th ed.), Am. Pub. Health Assoc., New York, 1936.

[77] I. L. Ouzdina and N. F. Blajek, *Chimie & Industrie*, *37*, 1096 (1936).

as described above, omitting the use of sodium citrate. This makes the color changes sharper because of the absence of the citrate buffer. Saturate the cold solution with hydrogen sulfide. Filter and wash well. Dissolve the sulfides in 5 ml. of hydrochloric acid (1:1) and 20 ml. of water. Slowly saturate the cold solution with hydrogen sulfide and filter. Copper alone is precipitated and the zinc is in the filtrate. Evaporate the filtrate to dryness and dissolve the residue in 4 to 5 drops of hydrochloric acid (1:1) and a little water. If necessary warm slightly before the addition of water. Transfer to a 25-ml. volumetric flask and make to volume. To an appropriate aliquot, usually 5 or 10 ml. of this solution, add 10 ml. of 0.1341 *N* potassium hydroxide, standardized against potassium hydrogen phthalate. Carefully neutralize the excess potassium hydroxide with 0.1 *N* hydrochloric acid, using phenolphthalein as indicator, and then add exactly 1 ml. of acid in excess. Transfer to a 50-ml. Nessler tube. Dilute with water to 45 ml., add 1 ml. of 2 per cent potassium ferrocyanide solution, mix thoroughly, and make to volume. The solution is 0.002 *N* with respect to acid, and 0.0268 *M* with respect to potassium chloride. The nephelometric standards in Nessler tubes should be prepared in exactly the same way in order to insure that the ionic strength is the same in the standards and in the unknown. The most suitable range for comparison is that of standards containing 0.20 to 0.25 mg. per 50 ml. matched against solutions of the unknown of nearly the same opacity. The standards for comparison should vary from 0.25 to 0.50 mg. of zinc in steps of 0.05 mg. They may be prepared from ignited zinc oxide as directed in a preceding paragraph.

b. Dithizone Method[78,79]

The dithizone method provides a fairly rapid means of estimating zinc. After trapping the zinc-bearing dust by means of an impinger, the zinc may be brought into solution as described for lead on page 213. The solution is made alkaline with ammonia, a chloroform solution of dithizone is added, the mixture is shaken, and then permitted to stand and separate. If zinc is present, it combines with the dithizone in chloroform and colors it red. The intensity of the color is proportional to the amount of zinc, which should be kept within the range of 0.001 to 0.010 mg. In the method detailed below, the zinc is extracted with the lead, the total amount of dithizone is estimated titrimetrically, and the amount of zinc is calculated by subtracting the volume used in the lead determination.

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[78] P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed., 9,* 127 (1937).
[79] S. Mosgowitz and W. J. Burke, *N. Y. State Ind. Bull. 17,* 492 (1938).

Reagents. The reagents are prepared as directed in the method for lead, page 212.

Procedure. Transfer an aliquot of the solution prepared as directed on page 213, containing less than 25 micrograms of zinc or the equivalent of zinc and lead, to a 125-ml. separatory funnel. Do not add potassium cyanide solution. Note, however, that if copper is present, it will be extracted along with the zinc and lead, and consequently the method should be modified as detailed below.

Add 5 ml. of chloroform and small portions of dithizone. Shake and continue the addition of dithizone until it is present in excess. Draw off the chloroform layer and wash the aqueous phase with a small portion of chloroform containing a few drops of dithizone solution. Combine the chloroform layers.

Wash the chloroform layer at least twice with 3 volumes of dilute ammonium hydroxide solution in each washing. To break the emulsion that may form with the first washing, draw off the clear portion of the chloroform, as formed on standing. Add 1 ml. of chloroform and invert the separatory funnel several times gently. Again draw off the clear chloroform layer as it forms. After the major portion of chloroform has been withdrawn, add an additional 1 to 2 ml. and repeat as above. Avoid too many washings, since some free dithizone will distribute itself between the aqueous and chloroform phases. The chloroform extract should be bright red and should have no free dithizone. The last wash of ammonia water should be colorless.

Shake the chloroform layer with 2 volumes of 1 per cent hydrochloric acid vigorously in order to break the zinc and lead complexes. Draw off the dithizone solution, add half its volume of 0.5 per cent potassium cyanide solution, and titrate with the same standard lead solution as used for the determination of lead (page 214) in exactly the same way. Subtract the volume of standard lead solution equivalent to the amout of lead found in an equal aliquot as that taken for the zinc determination from the volume found above, representing both zinc and lead. Multiply this difference by 3.15 to give the quantity of zinc in micrograms present in the aliquot taken for analysis.

Blank analyses should be run using the water and reagents used in the analysis, and the result should be subtracted from the results obtained in the regular analysis to get the corrected results.

Copper Interference. To remove copper, which will be an interference in the lead and zinc determination, since copper will also be extracted by dithizone in the absence of cyanide, the test solution must be treated with successive acid and alkaline washes.

Shake the chloroform extract with twice its volume of 1 per cent hydrochloric acid. Repeat the acid extraction. If copper is to be estimated (page 288) retain the chloroform layer, otherwise it may be discarded. Adjust the pH to 8 with ammonium hydroxide solution (1:1), using phenol red as the indicator. Re-extract the zinc, lead, and any residual copper with an excess of dithizone solution and repeat the acid extraction. Adjust the pH to 8, extract again with excess dithizone solution, and wash out the excess dithizone with dilute ammonium hydroxide solution. Decompose the zinc and lead complexes with hydrochloric acid, and titrate the liberated dithizone with standard lead solution in the presence of potassium cyanide.

c. Sulfide Method[80]

The foregoing methods have been detailed for the estimation of small quantities of zinc. Larger quantities of zinc may be estimated by the sulfide method. In this procedure the zinc is separated from the other metals by first precipitating the metals having sulfides insoluble in relatively high acid concentration, the zinc remaining in the filtrate, and then determining the zinc by precipitating it as zinc sulfide in a buffered faintly acid solution, thus separating the metal from those other metals whose sulfides are soluble in faintly acid solution.

Often this determination is made after estimation of copper. Boil the filtrate from the copper separation to expel the hydrogen sulfide and reduce the volume to 250 ml. Add a drop of methyl orange indicator, 5 g. of ammonium chloride, and make alkaline with ammonium hydroxide. Add hydrochloric acid (1:9) dropwise to faintly acid reaction, add 10–15 ml. of sodium or ammonium acetate, 50 g. of salt made up to 100 ml. with water, and pass in hydrogen sulfide until precipitation is complete. Allow the precipitate to settle, filter, and wash twice with hydrogen sulfide water. Dissolve the precipitate on the filter with a little hydrochloric acid (1:3), wash the filter with water, boil the filtrate and washings to expel hydrogen sulfide, and cool. Add a distinct excess of bromine water. Add 5 g. of ammonium chloride and then ammonium hydroxide until the bromine color disappears. Add hydrochloric acid (1:3) dropwise until the bromine just reappears. Then add 10–15 ml. of sodium or ammonium acetate solution and 0.5 ml. of ferric chloride solution, 10 g. $FeCl_3.6H_2O$ in 100 ml. of water, or enough to precipitate the phosphates. Boil until all the iron is precipitated. Filter while hot and wash the precipitate with water containing a little sodium acetate. Pass hydrogen sulfide into the combined filtrate and washings until all the zinc sulfide, which should be pure white, is precipitated. Filter through a weighed, prepared Gooch crucible and wash with hydrogen sulfide-ammonium nitrate water. Dry the crucible, ignite at a bright red heat, cool, and weigh as zinc oxide, ZnO. Calculate the weight of metallic zinc, using the factor 0.8034.

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[80] *Methods Assoc. Official Agr. Chem.* (6th ed.), (1945).

Zinc sulfide sometimes forms colloidal precipitates that will not flocculate and consequently pass through the filter. Caldwell and Moyer[81] recommend the addition of a solution of gelatin, containing from 0.5 to 2 mg. of gelatin of very low ash content. The gelatin solution will produce instantaneous and complete flocculation of as much as 0.3 g. of zinc sulfide in 300 ml. of solution.

J. COPPER

Poisoning from copper fumes is undoubtedly rare because of the high boiling point of copper (melting point, 1083° C., and boiling point, 2310° C.). It has been previously mentioned that copper oxide may be a cause of metal-fume fever, although in this instance most cases are very likely due to zinc fumes rather than to copper when these metals occur together as in brass and the so-called commercial bronze, or red brass. There are some authorities who maintain that chronic copper poisoning is associated with a definite disease.[82,83] The views on copper as a poison have undergone changes and it is now accepted that minute amounts of the metal are necessary for proper human metabolism. Undoubtedly larger amounts of copper have a deleterious effect, nor can inhaled copper compounds be considered in the same light as ingested copper.

Determination

Copper-bearing dusts may be trapped by methods previously detailed. Ignition ashing is suitable, when needed, if copper is to be estimated alone. If, however, other metals, much more volatile are to be determined and ashing is necessary, the wet-ash method is to be preferred.

a. Iodide-Thiosulfate Method

In the methods detailed, the copper is separated from other metals by means of a sulfide precipitation and it is subsequently estimated by the iodine liberated in the cupric-cuprous iodide reaction.

Prepare an acid solution of the copper-bearing material and pass in hydrogen sulfide for 15 or 20 minutes. Filter the precipitate through quantitative filter paper. Wash. Place the filter paper plus the precipitate directly into a 100-ml. flask—a squat flask with a wide mouth, customarily called a "fat" flask, is preferable—and add 3 to 4 ml. of concentrated sulfuric acid and 6 ml. of concentrated nitric acid. Place glass hooks on the flask and cover with a watch glass. If the resultant mixture is dark, add nitric acid until it is clear. Evaporate to 1 or 2 ml., cool, add 30 ml. of water and an excess of bromine water. Place the flask on the steam bath until the solution is colorless, after which cool and add ammonium hydroxide. In case iron or other metal yielding an insoluble hydroxide is present, filter and then evaporate off the ammonium hydroxide. A rough estimate of the amount of copper can be obtained from the blue color and the volume, at this point. Make acid with acetic acid and titrate with 0.01 *N* sodium thiosulfate solution in the presence of about 5 g. of potassium iodide and 1 to 2 ml. of 1 per cent starch solution.

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[81] J. R. Caldwell and H. V. Moyer, *J. Am. Chem. Soc.*, *57*, 2372 (1935).
[82] F. B. Mallory, *Am. J. Path.*, *1*, 117 (1925).
[83] F. B. Mallory, *Arch. Int. Med.*, *37*, 336 (1926).

As an alternative method,[84] dissolve the ash in hydrochloric acid, neutralize with ammonium hydroxide, add 5 ml. of sulfuric acid, dilute to 200 ml., and boil for 1 minute. Cautiously add 10 ml. of a hot, saturated solution of sodium thiosulfate and continue boiling for 5 minutes. Filter the precipitate, wash six times with hot water, and reserve the filter if desired for a zinc determination. Fold the filter paper, place in a crucible, and ignite in a muffle at 500° C. Treat the residue with 1 ml. of nitric acid (2:5) and dry on the steam bath. Add 20 ml. of water and an excess of ammonium hydroxide and heat until the copper salts dissolve. Transfer to a 100-ml. flask. Make acid to litmus with acetic acid (1:1) and add 1 ml. in excess. Boil for 1 minute and cool to room temperature. Add 2 g. of potassium iodide, dissolved in enough water to make the final solution 50 ml. and titrate the free iodine with 0.01 or 0.005 *N* sodium thiosulfate solution until the end point is nearly reached. Add 2 ml. of 1 per cent starch solution and continue titrating until the color is discharged.

b. Potassium Ethyl Xanthate Method

Very small amounts of copper may be estimated colorimetrically by either the potassium ethyl xanthate method or the sodium diethyldithiocarbamate method. Separate the copper from other metals as the sulfide. Dissolve in a drop of nitric acid, if possible, otherwise keep the nitric acid down to a minimum. Transfer to a 50-ml. volumetric flask and make to volume. Transfer a 5-ml. aliquot to a Nessler tube containing 10 ml. of a freshly prepared 0.1 per cent solution of potassium ethyl xanthate. Dilute to 25 ml. and mix. Place 10 ml. of the ethyl xanthate reagent into another Nessler tube. Dilute to 15 ml. Add from a 10-ml. semimicroburette, a drop at a time, while continually stirring, a standard copper solution containing 0.1 mg. of copper per ml. To prepare this standard, dissolve 0.3928 g. of copper sulfate, $CuSO_4.5H_2O$, in water, transfer to a 1-liter volumetric flask, make to volume, and mix. Continue the addition and stirring until the color in the tube containing the standard copper solution apparently matches the color of the unknown. Adjust the volume to 25 ml. and the color to match the test solution as closely as possible. Compute the quantity of copper from the volume of standard copper solution used.

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[84] *Methods Assoc. Official Agr. Chem.* (6th ed.), 1945.

c. Sodium Diethyldithiocarbamate Method[85,86]

After the copper has been separated as the sulfide, dissolve in a minimum amount of nitric acid. Evaporate almost to dryness to drive off excess acid if necessary. Dissolve in water, transfer to a volumetric flask, and make to volume. Take a 50-ml. aliquot, add 5 ml. of ammonium hydroxide solution (1:5), and filter if a precipitate forms. Transfer to a Nessler tube and add 5 ml. of a 0.1 per cent solution of sodium diethyldithiocarbamate [1 g. of sodium diethyldithiocarbamate, $N(C_2H_5)_2.CS_2Na$, dissolved in water and diluted to 1 liter]. Compare the color produced within 1 hour with that of standards treated the same way. The standards may be prepared by diluting 25 ml. of the 0.1 mg. of copper per ml. standard of the potassium ethyl xanthate method to 250 ml. This yields a solution containing 0.01 mg. copper per ml. Convenient standards contain from 0.005 to 0.05 mg. of copper.

d. Dithizone Method[87]

Copper may often be present along with lead and zinc, particularly in soldering operations that involve the heating of copper or copper alloys. It may be estimated in such mixtures by the dithizone method.

Wash the initial extract of lead, zinc, and copper dithizonates (see page 285) with dilute ammonium hydroxide solution to remove the excess free dithizone. Treat with 1 per cent hydrochloric acid and retain the aqueous layer for the estimation of zinc and lead. Shake the chloroform solution with half its volume of 0.5 per cent potassium cyanide solution and titrate with the standard lead solution (page 214). The presence of potassium cyanide makes it unnecessary to decompose the copper-dithizone complex by acid since this is done by the cyanide. The difference between the volume of lead solution used in this titration and that used for the titration of zinc and lead together, multiplied by

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[85] T. Callan and J. A. R. Henderson, *Analyst*, 54, 650 (1929).

[86] L. A. Haddock and N. Evers, *Analyst*, 57, 495 (1932).

[87] W. J. Burke, S. Moskowitz, J. Siegel, B. H. Dolin, and C. B. Ford, *Industrial A Analysis*, Division of Industrial Hygiene, N. Y. State Dept. Labor, New York, 1943

3.07, equals the quantity of copper, in micrograms, present in the aliquot taken for the analysis.

K. TIN

Very few industrial illnesses are directly traceable to tin. It has been shown that tin tetrachloride is irritating and has caused illness. This compound is used in the weighting of silk and as a mordant for dyeing. It is to be noted that it is the product that is produced when so-called tin plate, scrap tin-plated metal, is detinned with chlorine. Pedley[88] quotes the U. S. Bureau of Mines as saying that 8.5 parts per million in air caused coughing and that 1 part per million, 1 mg. per liter, caused death of mice in 10 minutes. However, Pedley himself found that guinea pigs could tolerate as much as 3 parts per million for months with no apparent ill effect. Organic compounds of tin such as tin tetramethyl have been found to produce illness.[89] Tin has a comparatively low melting point, 231.9° C., but it has a high boiling point, 2270° C. The high boiling point tends to minimize danger from fumes.

Determination

Tin-bearing dust may be sampled as previously detailed. A method for its separation as the sulfide and its subsequent estimation by titration with standard iodine solution has been indicated under the Section B, on antimony.

a. Sulfide Method

Tin may be precipitated as stannous sulfide and separated from sulfides insoluble in polysulfide by solution in polysulfide and filtration. The tin is then reprecipitated as the sulfide and estimated as the oxide after roasting.

If an acid digestion has been made, which is the preferable procedure if ashing is required when tin is being determined, because of the volatility of tin tetrachloride, add 200 ml. of water to the digested sample and transfer to a 600-ml. beaker. Rinse the Kjeldahl flask with three portions of boiling water, making a total volume of approximately 400 ml. If the tin has been brought into solution without the need of an acid digestion, dilute to approximately the same volume. Cool, and add ammonium hydroxide until just alkaline, then add 5 ml. of hydrochloric acid or 5 ml. of sulfuric acid (1:3) for each 100 ml. of solution. Place the beaker, covered, on a hot plate. Heat to about 95° C. and pass in a slow stream of hydrogen sulfide for 1 hour. Digest at 95° C. for another hour and allow to stand for $^1/_2$ hour longer. Filter, and wash the precipitate of stannous sulfide alternately with three portions each of wash solution and hot water. The wash solution consists of 100 ml. of saturated ammonium acetate solution, 50 ml. of glacial acetic acid, and 850 ml. of water. Transfer the filter and precipitate to a 50-ml. beaker, add 10–20 ml. of ammonium polysulfide, heat to boiling, and filter. Repeat the digestion with ammonium polysulfide and the filtration twice, and then wash the filter with hot water. Acidify the combined filtrate and washings with acetic acid (1:9), digest on a hot plate for 1 hour, allow to stand overnight, and filter through a double 11-cm. quantitative filter. Wash alternately with two portions each of the wash solution and hot water, and dry thoroughly in a weighed porcelain crucible. Ignite over a Bunsen flame, very gently at first to burn off the filter paper and to convert the sulfide to oxide, then partly cover the crucible and heat strongly over a large Meker burner. Weigh as stannic oxide, SnO_2, and calculate to metallic tin by using the factor 0.7877.

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[88] F. G. Pedley, *J. Ind. Hyg.*, *9*, 43 (1927).
[89] J. Seifter, *J. Pharmacol.*, *66*, 32 (1939).

b. Thioglycolic Acid Method

In this method[89a] the tin is separated as stannous sulfide, it is redissolved in sodium hydroxide solution, and after being made acid with hydrochloric acid, the color obtained with a reagent containing thioglycolic acid is compared against standards.

Convert the tin to stannous sulfide as described above and filter. Digest the paper and precipitate with 10 ml. of 10 per cent sodium hydroxide solution on the steam bath for at least 10 minutes. Filter and wash well. Make the solution just acid by adding concentrated hydrochloric acid, add 2 drops of thioglycolic acid and dilute to 100 ml. with water. Take an aliquot of 5 ml. in a boiling tube with 5 ml. of water, add 0.5 ml. of concentrated hydrochloric acid and 0.5 ml. of a reagent containing 0.1 g. dithiol and 0.25 ml. of thioglycolic acid dissolved in 50 ml. of 1 per cent sodium hydroxide solution. Immerse in a bath of boiling water for 30 seconds, allow to stand for 1 minute, and compare with standards treated similarly.

The reagent is best kept in an atmosphere of hydrogen but should be rejected as soon as a white precipitate of disulfide appears. It seldom keeps longer than two weeks.

[89a] R. De Giacomi, *Analyst, 65,* 216 (1940).

Tin may also be estimated colorimetrically by dissolving the purified stannous sulfide in 2.5 ml. of hydrochloric acid. Place this solution in a test tube fitted with a cork and delivery tube. Add a small piece of zinc and when it is dissolved pass in carbon dioxide to replace the air, add 2 ml. of 0.2 per cent dinitrodiphenylaminesulfoxide in 0.1 *N* sodium hydroxide solution. Boil the mixture for a few minutes and dilute to 100 ml. Add a few drops of ferric chloric solution. The violet color so obtained may be matched against standard solutions of tin treated the same way.

L. NICKEL

Nickel is an industrial hazard from three main sources: nickel plating and nickel salts such as nickel sulfate; nickel dust in grinding; and nickel carbonyl. Metallic nickel has been shown not to be poisonous as an inherent property.[90] Nickel carbonyl, on the other hand, is an extremely poisonous compound. Amor[91] states that it is relatively at least five times as toxic as carbon monoxide. It has been shown that a concentration of 0.018 per cent by volume of nickel carbonyl would kill a full-grown healthy rabbit after 1 hour of exposure.[92] Metallic nickel, in an extremely fine state of subdivision, may also give rise to fever.

Determination

a. Potassium Dithiooxalate Method[93-96]

Very small amounts of nickel may be determined by use of this method. The nickel is separated from iron and, if necessary, from cobalt. Its concentration is then determined by the formation of magenta-colored nickel dithiooxalate.

Samples may be collected by one of the many methods previously detailed. If necessary, evaporate, dry, and char the specimen in a porcelain dish. Ash at low red heat, being careful not to fuse the ash. Cool, add 15 ml. of hydrochloric acid (1:1) and sufficient water, if necessary, to cover the residue. Cover the dish with a watch glass and heat to boiling. Filter, and extract two more times with hot water. If a clean ash has not been obtained, return the filter paper and its residue to the original ashing dish, dry, and re-ash in a muffle. Extract as directed above. Combine all the filtrate-extracts and washings, and neutralize the hydrochloric acid with ammonium hydroxide, using methyl orange as indicator. Add a few drops of hydrochloric acid until the solution is just acid. Saturate the cold solution with hydrogen sulfide and allow to stand overnight. Filter and wash the precipitate with hydrogen sulfide water. Combine the filtrate and washings, which contain the nickel, and boil until free of hydrogen sulfide. Add bromine water to oxidize iron to the ferric state.

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[90] K. R. Drinker, L. T. Fairhall, G. B. Ray, and C. K. Drinker, *J. Ind. Hyg.*, *6*, 307 (1924).

[91] A. J. Amor, *J. Ind. Hyg.*, *14*, 216 (1932).

[92] H. W. Armit, *J. Hyg.*, *7*, 525 (1907); *8*, 565 (1908).

[93] H. O. Jones and H. S. Tasker, *J. Chem. Soc.*, *95*, 1904 (1909).

[94] L. T. Fairhall, *J. Ind. Hyg.*, *8*, 528 (1926).

[95] K. R. Drinker, L. T. Fairhall, G. B. Ray, and C. K. Drinker, *J. Ind. Hyg.*, *6*, 346 (1924).

[96] J. H. Yoe and F. H. Wirsing, *J. Am. Chem. Soc.*, *54*, 1866 (1932).

If cobalt is present, proceed as directed below. If cobalt is absent, it is necessary to free the solution only of iron, which interferes with the determination. To the cold, slightly acid solution, add 10 ml. of 50 per cent ammonium acetate solution and 0.5 ml. of glacial acetic acid. Under these conditions, iron is precipitated in the cold. Warming should be avoided to prevent reduction of iron to the ferrous state. Filter the cold solution through quantitative filter paper into a volumetric flask. Dilute to a known volume depending upon the nickel concentration. Transfer 50 ml. of this solution to a Nessler tube and add a small amount of potassium dithiooxalate. If nickel is present a clear magenta color develops at once. If nickel is absent no color will develop except a slight yellow.

Procedure in the Presence of Cobalt. If cobalt is present, it must be separated from the nickel. To do this both calcium and magnesium are precipitated as oxalate and phosphate respectively. Then nickel is isolated with α-benzildioxime and subsequently can be estimated as detailed above.

To the nickel solution, add 10 ml. of 20 per cent sodium citrate solution to prevent precipitation of iron. Add saturated ammonium oxalate solution to precipitate calcium. When precipitation is complete, add dilute ammonium hydroxide solution slowly to precipitate ammonium magnesium phosphate in the same solution. Filter. Dissolve the precipitates in hydrochloric acid and then reprecipitate calcium and magnesium as oxalate and phosphate as above. Filter and combine this filtrate with the main filtrate. This step recovers any nickel occluded on the calcium and magnesium precipitates. To the alkaline filtrate, add an excess of α-benzildioxime, filter the nickel precipitate, dissolve in aqua regia, and evaporate the acid solution to dryness in a porcelain dish. Dissolve in a few drops of dilute hydrochloric acid and make to volume in a volumetric flask. Determine nickel colorimetrically with potassium dithiooxalate.

Standards containing from 0.005 to 0.05 mg. of nickel can be prepared by dissolving a weighed portion of nickel dimethylglyoxime, which contains 20.32 per cent of nickel, in aqua regia, evaporating, redissolving in hydrochloric acid, evaporating again, redissolving in hydrochloric acid, and making up to a known volume. To prepare standards make further dilutions. Higher concentrations of nickel can be matched in a colorimeter.

b. Dimethylglyoxime Method

Larger quantities of nickel can be estimated by the dimethylglyoxime or α-benzildioxime methods. The analytical chemistry of the dioximes particularly as applied to nickel has been discussed by Diehl[97] and by Prodinger.[98]

Prepare an acid solution of the nickel salt. Filter, if necessary, and evaporate in a porcelain dish on a water bath. Dissolve the residue in 50 ml. of hot absolute alcohol, rendered just alkaline with ammonium hydroxide, and add 50 ml. of a hot saturated solution of dimethylglyoxime or α-benzildioxime. Heat the mixture for a few minutes on the bath and filter through a tared Gooch crucible, wash with hot alcohol, dry at 100° C., cool, and weigh.

If α-benzildioxime is used then the weight of precipitate multiplied by the factor 0.1093 equals the weight of nickel. If dimethylglyoxime is used then the weight of precipitate multiplied by the factor 0.2032 equals the weight of nickel.

Nickel Carbonyl

Nickel carbonyl, $Ni(CO)_4$, is a clear, straw-colored liquid, which boils at 43° C. It can be decomposed by heating to 150° C., at which temperature it breaks up into nickel and carbon monoxide. This is the basis for the Mond process of obtaining pure nickel.

Nickel carbonyl is a highly poisonous substance. The recommended maximum allowable concentration is 1 part per million. The concentration may be estimated by passing a known volume of air containing gaseous nickel carbonyl through a silica or heat-resistant glass tube heated to red heat.

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[97] H. C. Diehl, *The Applications of the Dioximes to Analytical Chemistry,* Iowa State College, Ames, 1940.

[98] W. Prodinger, *Organic Reagents Used in Quantitative Inorganic Analysis,* Elsevier New York, 1940.

The nickel deposits on the walls of the tube in the form of a mirror. The nickel may then be dissolved in sulfuric acid and determined by one of the methods outlined above. Nickel carbonyl may also be trapped in a bubbler containing aqua regia or sulfuric acid, after which the acid solution may be analyzed by an appropriate method.

M. IRON

1. Iron Carbonyls

Carbon monoxide forms volatile compounds with iron such as iron tetracarbonyl, $Fe(CO)_4$, and iron pentacarbonyl, $Fe(CO)_5$, when passed over iron, especially finely divided iron, at 40–80° C. They may be formed by the passage of illuminating gas through iron pipes. These compounds are only slightly less toxic than nickel carbonyl.[99]

These compounds may be trapped and decomposed by heat in silica or heat-resistant glass tubes in a manner entirely analogous to nickel carbonyl.[100-102] The iron deposited in the tubes may then be estimated by one of the usual methods.

If iron carbonyl can be obtained as an ether extract, it may be detected by dissolving 1 drop of the residue in methyl alcohol. Add perhydrol and 10 per cent sodium hydroxide solution. Dissolve the ferric hydroxide formed in hydrochloric acid and add 2 ml. of 10 per cent potassium thiocyanate solution. If iron carbonyl is present a red color is produced.

2. Iron Oxides

Iron oxide fume is generated in welding operations.[103,104] It has been shown that continued exposure to concentrations above 30 mg. per cubic meter may cause a chronic bronchitis. The recommended maximum allowable concentration is 15 mg. per cubic meter of air.

Iron oxide fume may be sampled by means of the electrical precipitator, although at times an impinger containing water has been used.[105]

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[99] A. J. Amor, *J. Ind. Hyg.*, *14*, 216 (1932).

[100] H. E. Roscoe and H. E. Scudder, *Proc. Chem. Soc.*, *7*, 126 (1891).

[101] R. H. Griffith and G. C. Holliday, *J. Soc. Chem. Ind.*, *47*, 311 (1928).

[102] G. Lunge and H. R. Ambler, *Technical Gas Analysis*, Van Nostrand, New York, 1934.

[103] A. M. Noyes, A. Tienson, G. W. Daubenspeck, L. Kirschner, and R. Rink, *Illinois State Dept. Labor, Tech. Paper 4* (1944).

[104] P. Drinker and A. G. Cranch, *U. S. Dept. Labor, Div. Labor Standards, Special Bull. 5* (1942).

[105] G. C. Harrold, S. F. Meek, and C. P. McCord, *J. Ind. Hyg. Toxicol.*, *22*, 347 (1940).

The iron in iron oxide fume is present principally in the ferric form. It may thus be estimated by titration with ceric sulfate, since

$$Ce^{++++} + Fe^{++} \longrightarrow Fe^{+++} + Ce^{+++}$$

Dissolve the fume in 15 ml. of hydrochloric acid (2:1) and reduce the iron to the ferrous state by use of 0.5 N stannous chloride solution in the usual way. Cool, dilute, and oxidize any excess stannous chloride by the addition of saturated mercuric chloride solution. Titrate with standard ceric sulfate solution, prepared by dissolving an accurately weighed amount of anhydrous ceric sulfate, $Ce(SO_4)_2$ (formula weight, 332.25), equivalent to the normality required in 500 ml. of 1 or 2 N sulfuric acid and diluting to 1 liter with water. Erioglaucin, eriogreen, *o*-phenanthroline-ferrous complex, and other substances may be used as the indicator.

N. BERYLLIUM

The relatively great increase in the use of beryllium and beryllium salts during World War II, particularly for the preparation of fluorescent powders and fluorescent lamps, focused attention on illness attributable to such compounds.[106] Beryllium metal and its ions are not considered poisonous but it may act as an adjuvant in certain instances. Beryllium sulfate dust readily hydrolyzes and the sulfuric acid locally produced may cause ulceration. The toxicology of beryllium has been reviewed.[107]

Colorimetric Determination

The amount of beryllium in dust may be estimated by its reaction with an anthraquinone derivative, 1,4-dihydroxyanthraquinone-2-sulfonic acid (quinizarin-2-sulfonic acid) to give a red color, which is proportional to the amount of beryllium present when buffered at pH 7.0 with ammonium acetate.

Dilute weakly acid solution of beryllium dust to a convenient volume. Remove phosphates, if present, by use of zirconium nitrate solution and remove the excess of zirconium by use of selenious acid. Adjust the hydrogen ion concentration of the filtrate to pH 3.5. To a 1-ml. aliquot of test solution add 5 ml. of 5 per cent ammonium acetate solution and 0.2 ml. of a 0.5 per cent aqueous solution of 1,4-dihydroxyanthraquinone-2-sulfonic acid. Allow to stand 5 minutes and compare in a visual colorim-

[106] L. T. Fairhall, *Ind. Hyg. Newsletter, 6,* No. 12, 7 (1947).

[107] F. Hyslop, E. D. Palmes, W. C. Alford, A. R. Monaco, and L. T. Fairhall, *U. S. Pub. Health Service, Nat. Inst. Health Bull. 181* (1943).

eter against the closest match of a set of standards containing from 0 to 10 micrograms of beryllium treated the same way.

O. PLATINUM

Exposure to complex platinum salts has been shown to cause symptoms[108] such as wheezing, coughing, running of the nose, tightness of the chest, shortness of breath, and cyanosis. This indicates that such atmospheres should be carefully controlled.

Traces of platinum in the air may be estimated spectrographically.[109]

P. PALLADIUM

Palladium and palladium salts are used chiefly in the electrical industry and in dentistry. The toxicology of palladium and methods of analysis have been reviewed by Meek, Harrold, and McCord.[110]

Q. INDIUM

Investigations of the toxicity of indium have shown that it possesses potentially highly toxic properties.[111] Silver ornaments plated or diffused with indium appeared to have no irritant action. A method for the determination of indium in food and feces is described by these investigators.[112]

R. COBALT

The toxicology of cobalt from an industrial-hygiene point of view has been reviewed by Fairhall.[113] The use of cobalt industrially has increased within the past decade, principally in sellite-, carbide-, and Alnico-type alloys. It is also used as a bonding material in the preparation of tungsten carbide. While the toxicity of cobalt by mouth is low, indeed it has been shown that cobalt is a micronutrient particularly for sheep and cattle, cobalt salts have been shown to cause polycythaemia in animals, and powdered cobalt produces dermatitis.[114]

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[108] D. Hunter, R. Milton, and K. M. A. Perry, *Brit. J. Ind. Med.*, *2*, 92 (1945).

[109] S. J. R. Fothergill, D. F. Withers, and F. S. Clements, *Brit. J. Ind. Med.*, *2*, 99 (1945).

[110] S. F. Meek, G. C. Harrold, and C. P. McCord, *Ind. Med.*, July, 1943.

[111] C. P. McCord, S. F. Meek, G. C. Harrold, and C. E. Heussner, *J. Ind. Hyg. Toxicol.*, *24*, 243 (1942).

[112] G. C. Harrold, S. F. Meek, N. Whitman, and C. P. McCord, *J. Hyg. Toxicol.*, *25* 233 (1943).

[113] L. T. Fairhall, *Ind. Hyg. Newsletter*, *6*, No. 10, 6 (1946).

[114] L. Schwartz, S. M. Peck, K. E. Blair, and K. E. Markuson, *J. Allergy*, *16*, 51 (1945).

Cobalt carbonyls are used as catalysts in the manufacture of motor fuels. The presence of these compounds in air may be detected by passing a known volume of air through a silica or heat-resistant glass tube heated to red heat. The cobalt deposits on the walls of the tube and may then be determined as detailed in the nitroso R salt method below. Very likely absorbers containing aqua regia or sulfuric acid can also be used to trap the cobalt carbonyl.

Determination

A method for the determination of cobalt in atmospheric dust samples of special steels, alloys, ores, and minerals has been developed by Keenan and Flick.[114a] The samples are collected by means of an electrostatic precipitator, the dust collected is weighed, fused, and an aliquot is analyzed by the nitroso R salt method.

Nitroso R Salt Method

Preliminary Treatment. Collect the dust by means of a direct current electrostatic precipitator using aluminum collecting electrodes. Upon receipt of the electrodes in the laboratory, remove the metal or Bakelite caps, wipe the outer surfaces of the electrodes clean with alcohol on a gauze pad, dry by wiping with a clean pad of dry gauze, and weigh after a 15-minute waiting period for equilibrium to take place.

Transfer the samples from the electrodes to Pyrex test tubes using a minimum amount of 30 per cent alcohol, usually 10–20 ml. is adequate, with the aid of a rubber policeman. Dry the inner surface of the electrode by forcing through a dry pad of gauze, clean the outer surfaces again as before, and weigh after a 15-minute waiting period. The weight of the sample is the difference between the weighings.

Evaporate the samples to dryness in an oven at 105° C. and thus concentrate each sample at the bottom of the test tube.

Fusion Treatment. Carbides such as obtained from samples of cemented tungsten carbide may be decomposed by fusion with potassium peroxydisulfate to give a clean white or yellowish-white melt in 3 to 4 minutes by heating with a Meker burner.

Heat the samples with a Meker burner to remove any free carbon. Cool, add a sufficient amount of potassium peroxydisulfate, $K_2S_2O_8$, and heat gently at first and then more strongly, while rotating the tube at an angle to permit the molten peroxydisulfate to come in contact with and to decompose the carbides.

[114a] R. G. Keenan and B. M. Flick, *Anal. Chem., 20,* 1238 (1948). R. S. Young, E. T. Pinkney and R. Dick, *Ind. Eng. Chem. Ed., 18,* 474 (1946).

By this treatment cobalt, nickel, and titanium are converted to their sulfates, tungsten is converted to potassium tungstate, and tantalum and columbium to the oxides or tantalates and columbates.

Allow to cool, and dissolve the melt in hot water. Add 5 ml. of 6 *N* hydrochloric acid and dilute to 25 ml. with water. If the samples are heavy, dilute to 50 or 100 ml. Tungstic acid and hydrolyzed titanium salts may precipitate during the dilution but cobalt remains in solution in the 1.2 *N* hydrochloric acid.

Standard Cobalt Solution. Dissolve 0.0249 g. of cobalt oxalate, CoC_2O_4, in 10 ml. of 6 *N* hydrochloric acid and dilute to 1000 ml. with water. Transfer 100 ml. of this solution to a liter volumetric flask, add 10 ml. of 6 *N* hydrochloric acid, and dilute to volume. One ml. of this standard solution is equivalent to 0.001 mg. of cobalt.

Procedure. Transfer a suitable aliquot portion of the prepared sample after thorough mixing of the insoluble residue of tungstic acid, if any is present, to a beaker. Filter, if necessary, and wash three times with water. Evaporate the filtrate almost to dryness, add 2 ml. of concentrated nitric acid, and evaporate to dryness. Dissolve the sample by boiling in 10 ml. of water and 2 ml. of 6 *N* hydrochloric acid. Neutralize the sample with 20 per cent sodium hydroxide solution using phenolphthalein as indicator. Add 2 ml. of Spekker acid (prepared from 150 ml. of phosphoric acid, sp. gr. 1.75, and 150 ml. of sulfuric acid, sp. gr. 1.84, diluted to 1 liter with water), 10 ml. of 0.1 per cent aqueous solution of nitroso R salt, and 10 ml. of 50 per cent sodium acetate trihydrate (W/V solution). Bring the mixture to a vigorous boil, add 5 ml. of concentrated nitric acid, and boil the mixture for 1 to 2 minutes. Cool, dilute to 100 ml. with water and obtain the optical density difference between the test solution and a reagent blank balanced at zero on a Coleman Universal spectrophotometer at 510 mμ. Estimate the amount of cobalt from a standard curve graph of optical density against concentration, prepared from a series of 0- to 0.500-mg. cobalt standards carried through the same procedure.

S. BARIUM

Barium salts are used in substantial amounts in about twenty industries, among which may be mentioned the manufacture of dyes, paints, chemicals, insecticides, linoleum, explosives, and incendiary bombs. The soluble salts of barium are poisonous when ingested. Barium salts may cause dermatitis and loss of hair, as well as gastric symptoms, for these have been reported in industrial poisonings. The recommended maximum allowable concentration is 0.5 mg. per cubic meter.

Determination

The customary method for estimation of barium is precipitation as barium sulfate. Yagoda has developed a method for the estimation of barium[115] in atmospheric dusts that depends upon the fact that when barium sulfate is precipitated from solutions containing potassium permanganate, a marked pink color is imparted to the precipitate. In addition Yagoda uses his system of confined spot tests[116] and a special sampling bottle.

Sampling. Add 10 ml. 5 per cent nitric acid to 30-ml. Pyrex bottles (Fig. 85A) equipped with inverted ₮ 19/22 stoppers and bubbling tubes. Adjust the bubbling tube when ready to sample and pass 30 to 45 liters of air through at a rate not exceeding 3 liters per minute. Wash down any dust collected on the bubbling tube with 1–3 ml. of 5 per cent nitric acid, running the acid through the funnel-shaped opening of the tube. Close the bottle with the cap and fasten with broad rubber bands.

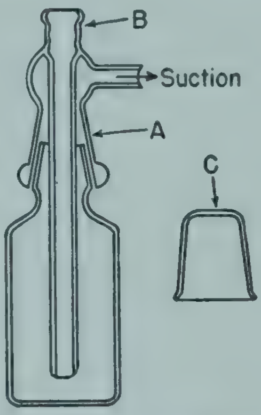

Fig. 85A. Sampling bottle. A. Bubbling tube with ₮ 19/22 inverted stopper. B. Entrance for sampled air. C. ₮ 19/22 cap.

Preparation of Sample. Transfer the sample to a No. 9 Coors low-form porcelain crucible and evaporate almost to dryness on a steam bath. Rinse the sampling bottle with 1–2 ml. concentrated nitric acid and transfer the rinse to the crucible. Add 1 drop of 20 per cent potassium nitrate solution and evaporate to dryness. Treat the residue with 1 ml. of an ash aid consisting of 0.5 per cent of magnesium oxide dissolved in concentrated nitric acid and evaporate to dryness. Heat the dry crucible over a small flame until the evolution of nitrogen oxides stops. When cool the residue should be white; if not add 0.5 ml. of nitric acid, evaporate to dryness again, and reignite.

Dissolve the residue in a few drops of nitric acid and evaporate again almost to dryness on a steam bath. Add 1 ml. of 10 per cent potassium carbonate solution and evaporate to dryness. Digest the residue on the steam bath with 5 ml. of water until all the caked matter is in suspension. Filter the precipitated magnesium carbonate carrying the trace of coprecipitated barium carbonate into a 3-ml. sintered-glass filter funnel of porosity M by use of an eye-dropper pipette with a rubber nipple of 0.2–0.3-ml. displacement. Wash the crucible with several 1-ml. portions of water until the wash water is free of alkali, using phenolphthalein solution as indicator. This washing is made more efficacious by repeatedly sucking the wash water into the tube and ejecting it against the walls of the crucible before transferring it to the funnel.

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[115] H. Yagoda, *J. Ind. Hyg. Toxicol., 26,* 224 (1944).

[116] H. Yagoda, *Ind. Eng. Chem., Anal. Ed., 9,* 79 (1937).

Add 0.5 ml. of 5 per cent nitric acid to the washed crucible, warm on the steam bath, and transfer to the filter containing the bulk of the carbonates. Support a 2-ml. precipitation tube, requiring a No. 9 ground-glass stopper, beneath the stem of the funnel and after the magnesium carbonate is completely dissolved apply suction. Wash the crucible and funnel with several 0.3-ml. portions of water until the 2-ml. mark is almost reached. Cool to room temperature and adjust the volume carefully to 2 ml.

Reagents. Primary Standard. Dissolve 89.0 mg. of barium chloride, $BaCl_2.2H_2O$, in water and dilute to 1 liter. This solution contains 50 micrograms of barium per ml.

Recrystallized Potassium Permanganate. Dissolve 20 g. of potassium permanganate, $KMnO_4$, in 100 ml. of water, bring to boiling, and allow to simmer for 10 minutes. Filter the hot solution through a sintered-glass funnel of porosity M to remove hydrated manganese oxides and cool the filtrate rapidly by rotating the flask under a stream of tap water. When cold, filter off the crystals on a sintered-glass funnel, drain by suction, and dry the crystals in an oven at 105° C. Hold in a glass-stoppered bottle.

Potassium Sulfate. Grind fine crystals of potassium sulfate, K_2SO_4, to pass through an 80-mesh sieve. Separate the 80–100-mesh fraction by rejecting the fines passing through a 100-mesh sieve.

Precipitating Reagent. Mix equal parts by weight of recrystallized potassium permanganate and the 80–100-mesh potassium sulfate.

Reducing Solution. Dissolve 15 g. of tartaric acid in 30 ml. of water, cool, and add slowly with intermittent cooling 10 ml. of concentrated sulfuric acid. Dilute to 50 ml. and transfer to a dropping bottle. Note the number of drops equivalent to 0.3 ml. of solution. The reduction of the permanganate is not instantaneous. The reaction starts about 1 minute after the addition of the reducing solution and is completed about 3 minutes after the initial evolution of carbon dioxide.

Precipitation. Add 100 mg. of the powdered potassium permanganate-potassium sulfate mixture to the test solution prepared as above, stopper the tube, and mix by inverting slowly for a period of 1 minute. At the end of a 2-hour digestion period at room temperature, decolorize the permanganate by the addition of 0.3 ml. of reducing solution. Prepare a series of standards containing 150, 75, 50, 25, 10, and 5 micrograms of barium by transfer of suitable aliquots of the primary standard to precipitation tubes and dilute to the 2-ml. mark. Treat as above.

Filter the pink mixed crystals on C. S. S. No. 598 confined-spot-test papers, wash with water, and dry at room temperature. Compare with the standards in a field of uniform illumination. Small quantities are compared best under reflected light and larger quantities by transmitted light. The latter is done by immersing the papers in a Petri dish containing carbon tetrachloride.

The intensity of the mixed barium crystals is reduced by calcium and strontium ions. When the lead:barium ratio exceeds 1:2, lead must be separated before the barium is estimated. Large amounts of trivalent iron interfere.

T. ALKALIES

Alkalies which have an industrial-hygiene significance are calcium hydroxide and oxide, barium hydroxide and oxide, sodium and potassium hydroxide, and sodium carbonate. These substances may cause dermatitis and conjunctivitis. Sodium and potassium hydroxides are extremely caustic and may cause severe and even fatal burns. Barium is also poisonous.

The alkalinity of the dust caused by these substances or, in general, of alkali-bearing dusts, fumes, and mists can be estimated by trapping the dust fume or mist in a known volume of standard acid, usually 0.02 *N*, and then determining the excess acid by back-titration with standard alkali solution. Sometimes water is used as the trapping medium and at times the *p*H of this is obtained. These may be sufficient for industrial-hygiene purposes. If further information is desirable, calcium may be determined as the oxalate, barium as the sulfate, sodium as the magnesium or zinc uranyl acetate complex, and potassium as potassium cobaltinitrite. For the details of these methods, the reader is referred to some of the texts listed at the end of the chapter.

U. RADIOACTIVE SUBSTANCES

The development of nuclear energy and its possible utilization for industrial purposes has presented industrial hygienists with a problem of the first magnitude. It is beyond the scope of this text to discuss the problem adequately. The control of radioactivity hazards is discussed by Sullivan[117] and by Morgan.[118] These hazards arise from exposure to fast and thermal neutrons, gamma rays, x-rays, beta rays, alpha rays and emitters of alpha rays, and radioactive fission products. The hazards, particularly in the last instance, can be considered as (1) external radiation effects; (2) internal effects in the lungs and gastrointestinal tract following inhalation and ingestion; and (3) effects produced after absorption by the body tissues of radioactive material present in the blood stream as a result of prior inhalation, ingestion, penetration through the skin, or injection through cuts and wounds of such radioactive material.

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[117] W. H. Sullivan, *Chem. Eng. News*, *25*, 1862 (1947).

[118] K. Z. Morgan, *Chem. Eng. News*, *25*, 3794 (1947).

Before the development of nuclear energy, exposure of industrial workers to radioactive substances occurred chiefly in the luminous paint industry. Luminous paint is made from zinc sulfide crystals which have been made radioactive by the addition of radium compounds. Sometimes mesothorium is added when a cheaper paint is desired, although this substitution is diminishing. The dry materials are mixed with oil and a thinner, sometimes with shellac or varnish, or with an adhesive such as gum arabic and water. It is probable that other radioactive material will be made available for this purpose. Luminous paint is used for watch and clock dials, gauge and other indicating dials on airplanes and automobiles, on scientific instrument panels, for glass drops on lamp indicators, and for house and Pullman-berth numbers and the like.[119,120] Thorium compounds are radioactive and several instances of illness have been described as arising from this source.[121]

Physicians, dentists, and technicians using radioactive materials for fluoroscopy and radiography are also exposed but it has been suggested that the term radium poisoning should be limited to those conditions in which radium, mesothorium, or other radioactive substances are ingested, inhaled, or have been injected, and should not include untoward results from exposure to external radiation. This is a debatable definition.

The first symptoms are generally skin disorders, burns, ulceration of the skin, trouble with the teeth, and the like. Later symptoms are blood disorders with severe anemia, lung disorders, and bone disorders such as necrosis and suppuration of the bones, especially the jaw bone.

The tolerance recommended for total or limited body exposure is 0.1 r. e. m. for a 24-hour period. The roentgen equivalent man, or r. e. m., is defined as that quantity of radiation which, when absorbed by

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[119] M. M. McMahon, *N. Y. State Ind. Bull.*, *16*, No. 7, (July 1937).

[120] L. Schwartz, F. L. Knowles, R. H. Britten, and L. A. Thompson, *J. Ind. Hyg.*, **15**, 362 (1933).

[121] L. T. Fairhall, *Ind. Hyg. Newletter*, 7, No. 2, 6 (1947).

man, produces an effect equivalent to the absorption by man of 1 roentgen of x- or gamma radiation. Sullivan points out that it is undesirable to work in radiation fields of greater than 1 roentgen per hour, which gives an exposure time limit of 6 minutes.

Since fast neutrons are about five times as damaging as x- or gamma rays, the tolerance set at the Clinton National Laboratory for this type of radiation was 20 mr. e. p. The roentgen equivalent physical, or r. e. p., is the intensity of radiation such that it may be absorbed at the rate of 83 ergs per gram of tissue. An r. e. p. becomes a roentgen if the radiation is x or gamma and the absorption takes place in air. The tolerance or maximum permissible exposure to radiation adopted at the Clinton National Laboratory is tabulated in Table 11A, and that of the Governmental Hygienists in Table 11B.

TABLE 11A

Maximum Permissible Exposure to Radiation[122]

Type of Radiation	Mr./day	Mr. e. p./day	Mr. e. m./day
X-Ray	100	100	100
Gamma	100	100	100
Beta	...	100	100
Fast neutron	...	20	100
Thermal neutron	...	50	100
Alpha[a]	...	10	100

[a] This alpha-tolerance level is considered only from the standpoint of internal irradiation effects.

TABLE 11B

Maximum Permissible Exposure to Radiation[122a]

Material or radiation	Radiant energy	Material or radiation	Radiant energy
Gamma (roentgen per day)	0.1	Thoron (curies per cubic meter)	10^{-8}
Radon (curies per cubic meter)	10^{-8}	X-ray (roentgen per day)	0.1

Detection and Determination

The monitoring of personnel, plant, equipment, and air so that exposure to dangerous concentrations of radioactive material is prevented is a difficult problem. The principal devices for the evaluation of radioactive hazards are electroscopes and Geiger-Müller counters. The latter consist of vacuum tubes in the form of an envelope containing copper or other metal cylinders charged negatively through which positively charged wires are stretched. The tubes contain neon, argon, helium, or krypton and ethyl ether or ethyl alcohol at very low pressure, the latter making the tube self-quenching. Energy of high radiation such as those mentioned in the previous discussion can penetrate the thin-wall glass window or envelope of such counters and can ionize or charge the neutral gas molecules. Sometimes thin windows of Lindemann glass, mica, or beryllium form one end of the envelope. The positive particles move toward the metal wall and the electrons move toward the charged wire, creating a pulse of electricity. This is amplified and each pulse may be counted. The intensity of radiation is measured by counting the pulses or by meter deflection. Morgan[123] does not recommend the use of Geiger-Müller counters for quantitative health-physics measurements.

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[122] Adopted at the Clinton National Laboratory.

[122a] Threshold limit values adopted by American Conference of Governmental Industrial Hygienists, 1948.

One type of device using the ionization method[123a] for measurement of individual exposure consists of a cylindrical ionization chamber about the size of a fountain pen, adequately insulated. In use, it is inserted in the bushing of the case of a string electrometer. In this way the central electrode of the ionization chamber is brought into contact with the rod extending from the insulated fiber of the electrometer. The central rod of the chamber and the fiber of the electrometer are brought to a definite voltage by an energy source inside the case through a contact key, and the corresponding reading of the electrometer serves as the zero of the instrument for dosage measurements.

The ionization chamber is now removed and can be carried by the individual while working. The ionization chamber is again connected to the electrometer at the end of the day and the deflection of the electrometer is noted. With a calibrated instrument, a direct reading of the exposure dose in roentgens can be obtained. The assumption made concerning this reading is that the decrease in voltage of the central electrode of the ionization chamber is entirely due to the ionization of the air in the chamber during the exposure period.

Alternative means of monitoring exposures to radioactive hazards are available. These are film badges containing films, sensitive to gamma, beta, and x-rays, sealed in a waterproof cover with a lead cross fastened to the outside of the badge.[124] The less penetrating beta rays will darken the film not protected by the lead, while the penetrating x- and gamma rays will interact with the lead, giving secondary radiations which will in turn affect the film underneath. After 1 or 2 weeks the density of the film is determined optically and compared with standard films so that the total ionizing radiation received by the wearer in that period can be estimated. Each lot of film must be calibrated.

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[123] K. Z. Morgan, *Chem. Eng. News.*, *25*, 3794 (1947).

[123a] L. F. Curtiss, in F. A. Patty, ed., *Industrial Hygiene and Toxicology*, Interscience, New York, 1948.

[124] D Holiday, *Ind. Hyg. Newsletter*, *7*, No. 8, 8 (1947).

Diamonds are highly sensitive to gamma rays and may be used to detect this type of radiation in the same way as a Geiger-Müller counter. When a diamond is placed in a strong electric field, it can initiate sharp electrical pulses when gamma radiation is absorbed.[125]

Bloomfield and Knowles[126] sampled atmospheric dust with the paper thimble. Single-thickness Whatman extraction paper thimbles, 100 by 25 mm., containing well-fluffed cotton wool to reduce clogging are suitable. The thimble is placed in an appropriate holder at the worker's breathing level, usually less than 1 foot from the face, and air is passed through the thimble at a rate of 2 cubic feet per minute, measured by a calibrated orifice meter or other device. Air samples of various sizes, from 60 to 200 cubic feet, should be taken at representative positions. The settled dust should also be sampled because it gives off emanations and radiation. At the Clinton National Laboratory, electrical precipitators were used for collecting suspended radioactive products from the air. A cylindrical aluminum foil was used to collect the dust and its activity was measured by alpha, beta, and gamma counters.

The thimbles or dust are ashed and the ash is fused with potassium acid sulfate, $KHSO_4$, and then analyzed electroscopically according to the method of Barker,[127] or as described by Roberts.[128]

Ives, Knowles, and Britten[129,130] used a Wulf electroscope for gamma-ray determinations and estimated thoron and radon with the Lind electroscope. Morgan[131] considers the fiber electroscope of the Landsverk-Wollan or Lauritsen types as a most reliable survey instrument.

To measure alpha-particle active dust such as emitted by uranium, plutonium, and radium, Carmichael and Tunnicliffe[132] suggest the use of a filter apparatus or a precipitator. The latter gives more consistent results and higher counts. Six hours is permitted to elapse after the

[125] *Chem. Eng. News, 25,* 3100 (1947).

[126] J. J. Bloomfield and F. L. Knowles, *J. Ind. Hyg., 15,* 368 (1933).

[127] H. H. Barker, *Ind. Eng. Chem., 10,* 525 (1918).

[128] L. D. Roberts, in N. H. Furman, *Scott's Standard Methods of Chemical Analysis,* Van Nostrand, New York (1939).

[129] J. E. Ives, F. L. Knowles, and R. H. Britten, *J. Ind. Hyg., 15,* 433 (1933).

[130] R. B. Moore, S. C. Lind, J. W. Marden, J. P. Bonardi, C. W. Davis, and J. E. Conley, *U. S. Bur. Mines, Bull. 212* (1923).

[131] K. Z. Morgan, *Chem. Eng. News, 25,* 3794 (1947).

[132] H. Carmichael and P. R. Tunnicliffe, *J. Ind. Hyg. Toxicol., 30,* 211 (1948).

collection of the samples in order to permit the natural alpha-particle activity of atmospheric dust to decay. Then the counts are made with a special counter[133] of the methane proportional type which only counts alpha particles even in the presence of strong beta-particle activity.

Neutrons, in contradistinction to alpha particles, protons, and beta particles, carry no electrical charge, hence, they do not ionize atoms directly as do charged particles. For this reason their concentration cannot be measured as are charged particles or x- or gamma rays. They do produce, however, secondary effects and consequently some measure of individual exposure can be obtained by an evaluation of these secondary effects. These are conditioned by the type of neutron and neutrons are classified for this purpose into two groups, fast neutrons and slow neutrons.

By making the walls of the ionization chamber, described above, of a material containing hydrogen atoms, such as Bakelite, the concentration of fast neutrons can be estimated, for though the fast neutrons have no charge, on collision with hydrogen atoms they give up much of their energy to the hydrogen atoms producing protons. The number of protons produced can then be measured.

Slow neutrons are very quickly absorbed by matter, resulting in production of new types of atoms with subsequent liberation of gamma and beta rays. When they impinge on the body, the radiations produced, principally gamma rays, can be measured by a device for evaluating gamma rays held close to the body.

For additional information on the estimation of exposure to radioactive material, the reader is referred to Curtiss[134] and to the symposium on nucleonics and analytical chemistry[135] sponsored by the Division of Analytical and Micro Chemistry of the American Chemical Society, in 1948.

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[134] L. F. Curtiss, in F. A. Patty, ed., *Industrial Hygiene and Toxicology,* Interscience, New York, 1948.

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CHAPTER IX

The Common Poisonous Compounds of Sulfur, Phosphorus, and Nitrogen; Oxygen and Ozone

The principal mineral acid gases and acids used in industry are compounds of sulfur, phosphorus, chlorine, fluorine, and nitrogen. Some of these acid gases are hazards because of use as such in industry. Others are hazards because they arise or are incidentally or accidentally produced during a step in the manufacture of a product. Examples of the former are the use of hydrofluoric acid in the etching of glass and the use of sulfur dioxide as a fumigant or refrigerant. Instances of the latter are the production of sulfur dioxide during the smelting of ores, the production of nitrous fumes during blasting or welding operations,[1] and the production of hydrogen sulfide during blasting operations in mines having sulfide-bearing rock.

The more usual type of hazard in the use of mineral acids is the one of acid burns resulting from splashing, spilling, spray, or other means of contact. Burns and dermatitis due to inorganic acids make up about 3 per cent of the total number of occupational dermatoses reported in the United States. In oil industries where oil is exposed to the action of sulfuric acid and in metal industries where "pickling" is done in open tanks, acid burns are a particular hazard.[2]

The more dangerous hazard from these acids is the inhalation of acid fumes and acid gases. Some of these provide a warning by odor, as, for instance, hydrogen sulfide, but even odor is not reliable for the nose becomes readily fatigued and accustomed to the odor within a short time, thus failing to warn. Others warn by setting up a reflex respiratory action, as in the case of sulfur dioxide, which is a practically irrespirable gas. Nitrogen oxide fumes have little warning effect and do not set up any reflex respiratory. This makes the possibility of breathing lethal amounts probable when gases of this type are inhaled.

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[1] William, *J. Ind. Hyg.*, *17*, **129** (1935).

[2] L. Schwartz, *U. S. Pub. Health Service, Bull, 249* (1939).

A. SULFUR

1. Sulfuric Acid

Sulfuric acid is the most widely used chemical compound. There is probably no manufactured article which does not have some part that has been treated with, or that comes into contact with, sulfuric acid. It was briefly explained that one of the dangers in the use of acid is acid burns. In the manufacture of sulfuric acid itself other dangers arise. There are two chief methods for the manufacture of sulfuric acid. One is known as the contact process, in which sulfur dioxide, very highly purified in order not to injure the catalyst, combines with oxygen in the presence of a catalyst such as finely divided platinum or ferric oxide to form sulfur trioxide, which is subsequently converted to sulfuric acid. The other method is known as the chamber process, in which process water vapor, sulfur dioxide, nitrous anhydride, N_2O_3, and oxygen react to form sulfuric acid. Actually, in the gaseous state nitrous anhydride breaks up to form nitric oxide, NO, and nitrogen tetroxide, NO_2. These gases act as the oxygen carrier and the reactants, steam, sulfur dioxide, nitrous anhydride, and oxygen, actually react to form nitrosylsulfuric acid, $HO.SO_2.ONO$, which subsequently breaks down to form sulfuric acid and nitrous anhydride again.

When the sludge of the lead chambers, in which this type of acid is made, is cleaned out, there is danger that these nitrous fumes will be released, for some of the nitrosylsulfuric acid crystallizes out on the walls of the chambers. The detection of such fumes will be discussed under the section on nitrogen acids.

Another danger in the manufacture of sulfuric acid by the chamber process is that due to arsine and hydrogen selenide. When iron pyrites (ferrous sulfide) is used to generate the sulfur dioxide by roasting, arsine and hydrogen selenide may be formed also because iron pyrites almost invariably contains as much as 1 per cent of arsenic or selenium sulfide. The liberation of these poisonous gases is thus an industrial hazard in this method, for these gases are not easily scrubbed out and must be driven off by heat.

Sulfuric acid is inhaled in the form of droplets; these attack the upper respiratory tract and, if breathed in sufficient quantity, cause death from edema or spasm of the larynx and inflammation of the upper respiratory tract.[3] The maximum allowable concentration recommended is 1.0 mg. per cubic meter.

Determination

Estimation of Sulfuric Acid and Sulfur Trioxide. In order to detect sulfuric acid spray or fumes of sulfur dioxide, the air may be passed through an absorber of the bubbler type or other trapping device containing a known quantity of standard sodium hydroxide solution, generally 0.02 *N*. After sampling has been completed, titrate the excess standard sodium hydroxide with an appropriate normality of standard hydrochloric acid to obtain the acidity. Water may also be used as the absorbing solution. In this instance the *p*H may be determined or the sample may be titrated with standard alkali solution. Acidify the solution with hydrochloric acid. Bring the solution to a boil and then precipitate sulfate with 10 per cent barium chloride solution. Digest on a hot plate for an hour or so, or allow to stand overnight in a warm place. Filter on ashless filter paper. Wash well with water. Transfer the filter and precipitate to a tared quartz crucible, dry, char, and ignite. Burn to a white ash in a muffle oven. Cool in a desiccator and weigh. The gain in weight may be considered barium sulfate.

Ives and his co-workers[4] estimated total sulfur in atmospheric dust by trapping the air containing the contaminants with a Greenburg-Smith impinger. To follow their method, transfer 50 ml. of the impinger solution to a beaker. Add 5 ml. of bromine water. Place on a steam bath and drive off the bromine. Evaporate to 10 ml. Add 1 ml. of *N* hydrochloric acid. Filter into a 150-ml. beaker. Wash the filter, catching the washings in the 150-ml. beaker, until the washings and solution total 75 ml. To the filtrate, add 2 ml. of 10 per cent barium chloride solution. Digest the precipitate on the steam bath for 2 hours. Allow to stand overnight. Filter on ashless filter paper, wash with water, and transfer the filter and its contents to a platinum or other crucible. Ignite, cool, and moisten with concentrated sulfuric acid. Drive off the excess sulfuric acid in an air bath. Reignite, allow to cool in a desiccator, and weigh. The additional weight is considered barium sulfate, from which weight the amount of sulfur can be calculated.

Tetrahydroxyquinone Method. A direct titration method has been developed for sulfates by Schroeder.[5] This method is based on the use of the specific indicator, tetrahydroxyquinone, for barium in the titration of sulfate. The tetrahydroxyquinone is used as an internal indicator. Sheen and Kahler[6] recommend the following details.

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[3] H. W. Haggard, *J. Ind. Hyg.*, *5*, 379 (1923–24).

[4] J. E. Ives, R. H. Britten, D. W. Armstrong, W. A. Gill, and F. H. Goldman, *U. S. Pub. Health Service, Bull. 224* (1936).

[5] W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, *5*, 403 (1933).

[6] R. T. Sheen and H. L. Kahler, *Ind. Eng. Chem., Anal. Ed.*, *8*, 127 (1936).

Reagents. Standard Barium Chloride Solution. The strength of this solution may vary from 1 ml., equivalent to 1 mg. of sulfate, to 1 ml., equivalent to 50 mg. of sulfate. The indicator is composed of disodium tetrahydroxyquinone ground with dried potassium chloride in a 1:300 ratio, and passing a 100-mesh screen. Ethyl alcohol or alcohol denatured by formula No. 30 or No. 3-A of the United States Treasury Department or isopropyl alcohol may be used as the diluent. Phenolphthalein indicator solution is used and also bromocresol green indicator solution if phosphates are present.

Procedure A. Carefully neutralize a 25-ml. aliquot of the sample solution containing up to approximately 2,000 parts of sulfate per million of solution with approximately 0.02 *N* hydrochloric acid until just acid to phenolphthalein. The temperature of the solution should be below 35° C. and it is advisable to work between 20 and 25° C. Add either 25 ml. of ethyl alcohol or one of the other solvents. Introduce the tetrahydroxyquinone, using 0.1 g. of the indicator for sulfate up to 100 parts per million and 0.2 g. for sulfate up to 2,000 parts per million. Swirl the flask to dissolve the indicator; the solution will be colored a deep yellow. Titrate with standard barium chloride solution, the strength to be employed depending on the approximate sulfate content of the sample. Add the standard barium chloride solution at a steady dropping rate with constant swirling of the flask, until the yellow color changes to a rose. The rose color is the end point and is due to the appearance of the red barium salt of tetrahydroxyquinone. The rose color should appear throughout the body of the solution and not as spots of color.

TABLE 12

Tetrahydroxyquinone Required for Various Sulfate Concentrations

Sulfate concentrations, ppm. of solution	Quantity of THQ indicator, gram	Strength[a] of $BaCl_2$ solution	NaCl required, grams
Up to 100[b]	0.1	1	
100 to 1,000[b]	0.2	1	
1,000 to 2,000	0.2	4	
2,000 to 4,000	0.4	10	2
4,000 to 10,000	0.4	10	4
10,000 to 20,000	0.6	50	8
20,000 to 30,000	0.8	50	8

[a] 1 ml. = mg. SO_4. [b] Subtract 0.1 ml. as a blank in titration.

Procedure B. (Sulfate range from 2,000 to 30,000 parts per million of the sample solution.) Add sodium chloride according to Table 12. The procedure is the same as in *A* for neutralization and titration.

Procedure C. (With phosphate up to 60 parts per million of the sample solution.) Carefully neutralize a 25-ml. filtered sample with approximately 0.02 *N* hydrochloric acid until just acid, yellow range, to bromocresol green, approximate pH 4. Follow the procedure as in *A* or *B*; no correction will be required for the phosphate ion present.

2. *Sulfur Dioxide*

Sulfur dioxide is one of the more important sulfur acid gases. Its use and production as a by-product in industry is enormous. Of course, its most significant use is in the manufacture of sulfuric acid, but very large quantities are also used in fumigation, bleaching, and refrigeration. Very large quantities are produced as by-products in the smelting of sulfur-bearing ores, the manufacture of paper by the sulfite process, and the manufacture of synthetic phenol. Its presence in the effluent gas from the combustion of sulfur-bearing coal makes it one of the more important causes of air pollution. In moist air, sulfur dioxide is converted to sulfuric acid and it is mainly in this form that it is found in air-pollution studies.

Sulfur dioxide (sulfurous anhydride, SO_2) is a colorless noninflammable gas with a suffocating odor. It boils at —10° C.; the liquid form has a specific gravity of 1.5 and its density with respect to air is 2.3. It is soluble in water, with the formation of sulfurous acid.

a. Physiological Response[7] and Toxicity

Sulfur dioxide is an irritant gas that is practically irrespirable to those unaccustomed to it. It readily elicits respiratory reflexes. It affects the upper respiratory tract but with deeper breathing affects the lower system also. Four parts per million can readily be detected by odor but as the nose becomes accustomed to it, the amount necessary to produce a reflex respiratory defense response increases. The minimum concentration causing irritation of the eyes is 20 parts per million; 8–12 parts per million will cause coughing. Jones, Capps, and Katz[8] found it impossible to remain in an atmosphere containing slightly less than 0.02 per cent of sulfur dioxide (200 parts per million) for more than 1 minute, because of eye irritation and the effect on the membranes of the nose, throat, and lungs. Lehmann[9,9a] found that 0.05 per cent in an atmosphere (500 parts per million) was dangerous to men exposed to it for periods of 30–60 minutes. This value would indicate that amounts greater than 0.1–0.2 per cent

[7] J. A. Holmes, E. C. Franklin, and R. A. Gould, *U. S. Bur. Mines, Bull. 98* (1915).

[8] G. W. Jones, J. H. Capps, and S. H. Katz, *Min. Sci. Press, 117*, 415 (1918).

[9] K. B. Lehmann in R. Kobert, *Kompendium der praktischen Toxikologie*, Enke, Stuttgart, 1912.

[9a] Y. Henderson and H. W. Haggard, *Noxious Gases*, Reinhold, New York, 1943.

(1,000–2,000 parts per million) might be fatal on continued exposure.[10] Fieldner,[10a] however, states that 0.2 per cent is intolerable but not dangerous. Other authorities give the concentration range which can be tolerated for exposures of 60 minutes as 50–100 parts per million, and the maximum concentration that can be tolerated for several hours without serious disturbances or with but slight symptoms as 10 parts per million. The latter concentration is generally accepted as the maximum allowable concentration.

b. Detection and Estimation

The literature on the detection and estimation of sulfur dioxide in air is very large. One of the reasons for the extensive literature is the adverse effect that sulfurous fumes have on the surrounding vegetation. Many air-pollution studies have been made in the neighborhood of smelters and in the neighborhood of other industries in which sulfur dioxide occurs in the effluent gas. Another important effect of sulfur dioxide is its corrosive action.

One of the methods used in an early air-pollution study was that of Marston and Wells described by the Selby Smelter Smoke Commission.[7] In this method a sample of air was drawn into a partially evacuated 20-liter bottle containing a solution of iodine colored with starch. Absorption of the sulfur dioxide was accomplished by vigorously shaking the bottle. The remaining iodine was titrated with thiosulfate solution.[11] This method has been modified by bringing the oxidized sulfur dioxide solution to the same intensity of blue as that of a blank by the addition of standard iodine solution.[12,13]

Iodine-Thiosulfate Method. Sulfur dioxide in air may be estimated by the following four methods. In the first, the sulfur dioxide is trapped in a standard solution of iodine in potassium iodide. The remaining iodine is then estimated by titration with standard thiosulfate.[14]

This method is used by a number of investigators. One variation is an apparatus[11] arranged for the automatic measurement of small concentrations of sulfur dioxide in air.

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[10] E. D. Gardner, S. P. Howell, and G. W. Jones, *U. S. Bur. Mines, Bull. 287* (1927)

[10a] A. C. Fieldner, *U. S. Bur. Mines, Inform. Circ. 6099* (1937).

[11] M. D. Thomas and R. J. Cross, *Ind. Eng. Chem., 20,* 645 (1928); M. D. Thomas, O. J. Ivie, J. N. Abersold, and R. H. Hendricks, *Ind. Eng. Chem., Anal. Ed., 15,* 287 (1943).

[12] R. J. McKay and D. E. Ackerman, *Ind. Eng. Chem., 20,* 538 (1928)

[13] C. E. Betz, J. H. Holden, and J. O. Handy, *Ind. Eng. Chem., 25,* 774 (1933).

[14] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem., 11,* 523 (1919).

In another variation, three special bubblers are arranged in series.[15] The first contains 10 ml. of 0.04 *N* iodine in potassium iodide solution, diluted with water to bring the solution to the proper height in the bubbler. The second absorber contains 2 ml. of 0.04 *N* sodium thiosulfate solution diluted with water. This absorber is used to catch any vaporized iodine from the first absorber. The third tube contains water to catch any sodium thiosulfate carried over mechanically from the second absorber. A known quantity of air is forced or drawn through the series of absorbers at a moderate rate. If aspirator bulbs are used they should be calibrated before use by means of a wet meter.

Transfer the iodine solution, thiosulfate solution, and water from the bubblers to a beaker. Titrate the remaining iodine with thiosulfate solution using starch as the indicator. To this result add the 2 ml. of standard thiosulfate solution used in the second bubbler. Titrate 10 ml. of the iodine standard solution with the thiosulfate solution. Subtract the first titration from the second. This yields the number of ml. of standard thiosulfate consumed by the sulfur dioxide.

In a simpler variation, pass the air through two bubblers, the first containing a known volume of 0.01 *N* iodine in potassium iodide solution and the second containing half that volume of 0.01 *N* sodium thiosulfate solution. Transfer the contents of both bubblers to a flask, wash twice with distilled water, add 1 ml. of starch indicator solution and titrate with 0.01 *N* sodium thiosulfate solution. Calculate the amount of sulfur dioxide present from the relationship that:

$$1 \text{ ml. } 0.01\ N\ I_2 \approx 0.1223 \text{ ml. } SO_2 \text{ at } 25^\circ \text{ C. and 760 mm.}$$

Hydrogen sulfide is also oxidized by iodine yielding hydrogen iodide:

$$SO_2 + I_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$$

and

$$H_2S + I_2 \longrightarrow 2HI + S$$

hence it will appear in the result as sulfur dioxide unless corrected for by a separate determination. This will be discussed in a separate section.

$$\text{Percentage of } SO_2 + H_2S \text{ present} = \frac{\text{Vol. sample [S.T.P.]}}{\text{ml. } Na_2S_2O_3 \times \text{value of 1 ml.}} \times 100$$

The net amount of sulfur dioxide equals this percentage minus the percentage of hydrogen sulfide found.

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[15] E. D. Gardner, S. P. Howell, and G. W. Jones, *U. S. Bur. Mines, Bull. 287* (1927).

Griffin and Skinner[16] described a portable apparatus for the determination of very small amounts of sulfur dioxide in air. Approximately 1 cubic foot of air is passed in about 4 minutes through 100 ml. of a 0.00003 *N* solution of iodine in potassium iodide and starch, in a bubbler or tower tube. At this dilution, practically no iodine is lost in the outgoing air stream. The exact amount of air passed through is measured by means of a Venturi meter. The sulfur dioxide trapped is subsequently evaluated by titration with 0.001 *N* sodium thiosulfate standard solution to a standard depth of color rather than to a colorless solution. They suggest the use of a soda lime tower in order to remove all sulfur dioxide at the source so that a blank can be run at the same time as the field test.

Hydrogen Peroxide Method.[17-19] The second method consists of trapping the sulfur dioxide in a bubbler containing hydrogen peroxide. The sulfuric acid may then be titrated with standard alkali, since in the oxidation sulfuric acid is formed from the sulfur dioxide, while the hydrogen peroxide decomposes to form water and therefore does not interfere in the titration. The sulfate formed may also be estimated gravimetrically by the barium sulfate method or titrimetrically by the tetrahydroxyquinone method described above. This method includes any sulfur trioxide that may be present in the air being sampled. If any is present, the iodine-thiosulfate method, page 314, or the iodine method, page 317, may also be used and the amount of sulfur trioxide may then be computed by difference. On the other hand, hydrogen sulfide does not interfere in this method, nor do other volatile sulfides.

Hydrogen peroxide generally contains free sulfuric acid. In order to free the peroxide from sulfate, start with 30 per cent hydrogen peroxide, dilute somewhat, neutralize with barium hydroxide solution, using bromophenol blue solution as indicator. After the reagent has settled in the cold, filter from the barium sulfate and determine the exact strength of the hydrogen peroxide by permanganate titration. Finally adjust to a 3 per cent strength. The bromophenol blue indicator remains unaffected for some time in the hydrogen peroxide solution.

Pass the air containing the sulfur dioxide through two absorbers, one containing 15 ml. of pure neutral 3 per cent hydrogen peroxide in 100 ml. of water and the other containing 5 ml. of the same reagent in 50 ml. of water. Alternatively, the free sulfuric acid may be estimated in the hydrogen peroxide, or to the sulfuric acid-free hydrogen peroxide a known quantity of standard sulfuric acid may be added. Known volumes of these reagents added to the bubblers will, of course, contain known quantities of acid. After sampling is finished, wash the contents of the second sampling bottle into the first absorber, if a titration can be performed in it. If not, wash the contents of both absorbers into a beaker or flask and titrate at room temperature with 0.1 *N* sodium hydroxide solution using bromophenol blue as indicator. The sodium hydroxide must be standardized with this indicator. Bromophenol blue is unaffected by carbon dioxide and also gives a distinct color change in cold hydrogen peroxide solution. One ml. of 0.1 *N* sodium hydroxide solution is equivalent to 3.2 mg. of sulfur dioxide, so that titration of small quantities of sulfur dioxide requiring less than 0.5 ml. of sodium hydroxide is not accurate. A gravimetric determination may be made after titration, the precipitation of barium sulfate being carried out at room temperature. After allowing the supernatant liquid to settle, filter and wash the residual barium sulfate three times by decantation with boiling water. Determine a blank on the reagents both by titration and gravimetrically and correct the results accordingly.

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[16] S. W. Griffin and W. W. Skinner, *Ind. Eng. Chem.*, *24*, 862 (1932).

[17] G. W. Monier-Williams, Ministry of Health, *Reports of Public Health and Medical Subjects*, No. 43, London (1927).

[18] M. D. Thomas and J. N. Abersold, *Ind. Eng. Chem., Anal. Ed.*, *1*, 14 (1929).

[19] M. D. Thomas, *Ind Eng. Chem., Anal. Ed.*, *4*, 253 (1932).

Iodine Method. Another method for the detection of small quantities of sulfur dioxide in air is detailed by Smith and Friis.[20] In this procedure the sulfur dioxide is trapped in standard sodium hydroxide solution which is subsequently acidified and the liberated sulfurous acid estimated by titration with standard iodine solution.

Fifty ml. of standard 0.1 *N* sodium hydroxide solution is placed in an absorption vessel of the Smith and Friis type or an appropriate known quantity of this reagent is placed in another suitable impinging or absorbing device. The aspiration is then carried forward until an adequate amount of air has been scrubbed through the liquid. The liquid is then drained from the Smith and Friis device, or poured from other devices into a glass-stoppered bottle. The absorption unit should be rinsed with two 5-ml. portions of water and the washings should be added to the sample in the bottle. If the analyses are to be subsequently performed in the laboratory, the stoppers should be sealed with wax.

Neutralize the sodium hydroxide solution with 6 ml. of *N* hydrochloric acid. Add 1 ml. of starch solution. Titrate with accurately standardized 0.001 *N* iodine solution until a blue end point is reached. Run a blank on the reagents used. The parts per million of sulfur dioxide present in the air may be computed by the following formulas:

$$1 \text{ ml. } 0.001\ N\ I_2 \approx 0.032 \text{ mg. } SO_2 \approx 0.0112 \text{ ml. } SO_2 \text{ at } 32^\circ \text{ F. } (0^\circ \text{ C.})$$

$$\text{Ppm. of } SO_2 = \text{No. ml. titrated} \times \frac{0.0112 \times (460 - \text{temp.}^\circ \text{ F.}) \times 10}{492}$$

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[20] R. B. Smith and B. S. T. Friis, *J. Ind. Hyg.*, *13*, 338 (1931).

When titrating more than 5 parts per million, it is best to use 0.01 N iodine, as a good end point cannot be obtained with 0.001 N iodine solution. The results of the formula should then be obtained by multiplying by 10.

Manganous sulfate can catalyze the oxidation of sulfur dioxide to sulfur trioxide. A 0.03 per cent solution may be used in an absorber to trap the sulfur dioxide. The resulting sulfuric acid can be determined by titrating the amount of iodine set free on the addition of potassium iodide and potassium iodate. This method is said to be able to detect as little as 0.1 part per million.[21]

Alkali Method. Pass the air to be sampled through a fritted bubbler containing N sodium hydroxide solution at a rate of 0.5 to 1 liter per minute. The amount of sulfur dioxide may then be estimated by one of the methods detailed above.

A simple variation of this method commonly used in the evaluation of the role played by sulfur dioxide in smog formation is to pass the air being sampled through standard sodium hydroxide solution, say 0.01 N, and then estimate the excess standard sodium hydroxide solution remaining by titration with standard acid. This method though rapid, has the disadvantage that all acidic components as well as sulfur dioxide are included in the result.

3. Hydrogen Sulfide

Hydrogen sulfide is a noxious gas that is extremely poisonous in very small quantities. It is the "stink damp" of miners. It has practically no use in industry but is an industrial hazard in many industries because it is a by-product or because it occurs accidentally. In almost every process where sulfur or sulfur compounds are used it is apt to be present. Burning silk and wool give off hydrogen sulfide and other noxious gases such as hydrogen cyanide, sulfur dioxide, ammonia, and carbon monoxide, some of which have a warning effect. In the Columbus penitentiary fire 320 lives were lost from this cause.[22] It is a hazard in the oil-refining industry, especially where high sulfur petroleum is being refined. Among other industries and places where hydrogen sulfide is a hazard may be mentioned mines, in which hydrogen sulfide is present naturally or in which blasting operations yield this gas, sewers, tanneries or other industries where animal matter is handled, the manufacture of sulfur dyes, the manufacture of artificial silk by the viscose process, and the rubber industry. In the viscose process for the manufacture of artificial silk, cellulose is treated first with sodium hydroxide solution and then with carbon disulfide. These reagents react to form sodium-carbon-sulfur compounds of the type of sodium thiocarbonate, Na_2CS_3, and $NaCS_2$, etc., which decompose in the spinning bath containing warm dilute sulfuric acid into sodium carbonate, Na_2CO_3, and hydrogen sulfide.

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[21] Y. D. Goldberg, *J. Applied Chem.* (*U.S.S.R.*), *7*, 1099 (1934); *Chem. Abstracts*, *29*, 5773 (1935).

[22] J. C. Olsen, G. E. Ferguson, and L. Scheflan, *Ind. Eng. Chem.*, *25*, 599 (1933).

a. Physiological Response and Toxicity[23]

In concentrations of 1 in 1,000 by volume or higher, hydrogen sulfide will cause immediate unconsciousness and will result in death unless artificial respiration is immediately applied. In such concentrations it is nearly as toxic as hydrogen cyanide and may act with equal rapidity by paralyzing the respiratory center of the brain. Hydrogen sulfide, however, differs from hydrogen cyanide as a poison in that it is not absorbed through the skin. In general its action depends upon its concentration and even a concentration of 0.005 per cent will cause poisoning. Hydrogen sulfide in such low percentage is often found in industry.[24] The effects of hydrogen sulfide for weaker concentrations may be summarized as follows:

Concentration in air		
Parts by volume	Mg. per liter	Effects
1 in 2,000	0.76	Very dangerous if inhaled for 15 to 30 minutes. Causes severe irritation of the eyes and respiratory tract with risk of pneumonia or serious injury to the lungs, which may readily prove fatal.
1 in 5,000	0.304	Dangerous if inhaled for 1 hour. Causes severe irritation of the eyes and respiratory tract. Eyes are affected after 6 to 8 minutes.
1 in 10,000	0.152	Symptoms of local irritation of eyes and respiratory tract after 1 hour exposure.

While hydrogen sulfide may be detected by smell, the sense of smell is lost in 2 to 15 minutes exposure to 0.010 to 0.015 per cent of this gas.

The maximum allowable concentration of hydrogen sulfide for an 8-hour exposure, as recommended by the American Standards Association,[24a] is 20 parts per million parts of air; this is equivalent to a concentration of 0.028 mg. per liter at 25° C. and 760 mm.

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[23] *Dept. Sci. Ind. Research Brit., Leaflet 1* (1937); *Analyst, 62,* 607 (1937).

[24] C. W. Mitchell and S. J. Davenport, *U. S. Pub. Health Service, Reprint 892* (1924).

[24a] *Am. Standards* Z37.2–1941.

b. Detection

Lead Acetate Test. The atmosphere to be tested may be sampled by means of a hand exhausting pump with a barrel approximately 1.25 inches in bore and a capacity of 126 ml. To the inlet end of the pump is screwed a spigot with an external screw to which a holder containing the test paper may be attached.

Test Papers. These may be made from Whatman No. 1 filter paper, cut into strips 2 by 4 inches. The strips are impregnated with lead acetate solution, 10 g. of lead acetate dissolved in 100 ml. of water plus 5 ml. of glacial acetic acid. They are then suspended vertically in an atmosphere free from hydrogen sulfide and left to dry at room temperature. One inch is cut off the top and bottom of each strip and discarded. These papers may be stored in a glass-stoppered, airtight container, in which a drying agent, such as a silica gel capsule is present.

Method. The lead acetate paper is clamped in a holder of special design (Fig. 13), which is screwed into the pump. The apparatus having been tested for leaks, a preliminary indication of the atmosphere to be tested is obtained by making 2 slow and steady strokes of the pump, and the paper is then removed from the holder and compared within 10 minutes with the standard color chart provided by the British Department of Scientific and Industrial Research. A positive test will be obtained if the concentration of the hydrogen sulfide is greater than 1 part in 60,000 (0.025 mg. per liter). If no stain has been produced, further tests are made with fresh lead acetate paper, this time increasing the number of strokes to 3 or 5. The concentration is read with the aid of the chart again. The stains obtained should be only on that side of the paper exposed to the gas entering the pump, and the back of the test paper should remain white or nearly so if the stain is very heavy. For sampling the gas from inaccessible places such as acid tanks or sewers, the observations of Chapter II apply.

It is clear that in the above method a known volume of air is drawn through the test paper. An alternative method of using lead acetate paper is the following.[25] The test paper is prepared by dipping filter paper into a solution containing 10 g. of lead acetate crystals in 100 ml. of 50 per cent glycerol. After removing the excess liquid with blotting paper, the strips of paper are placed in small glass tubes, which are drawn out, evacuated, and sealed. To test a sample of air or gas for hydrogen sulfide, connect the tube to the sample of air or gas by some suitable means, break off the end of the tube, and as a result of the air or gas entering the tube, the paper will react with the hydrogen sulfide in this small volume. By comparing the depth of color produced with that obtained with air or gas containing known volumes of hydrogen sulfide, the approximate hydrogen sulfide concentration can be established. By increasing the size of the ampoule, and by having the ampoules of known volume, this test can easily be applied in the field for the quantitative estimation of hydrogen sulfide.

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[25] P. Woog, R. Sigwalt, and J. de Saint-Mars, *Bull. soc. chim* [5] 2, 1214 (1935)

There are a number of automatic devices in which the quantity of hydrogen sulfide in air may be continuously recorded by impinging the air through a fine jet against a rotating drum on which is a chart of lead acetate paper. One of these devices is so arranged that the stain produced by the hydrogen sulfide causes a change in the optical transparency of a strip of paper that, in turn, interferes with a ray of light directed on a photoelectric cell and causes a bell to ring.[26]

Silver Cyanide Detector.[27] The U. S. Bureau of Mines has developed a detector that provides a simple and fairly accurate means of detecting hydrogen sulfide. It is rapid in giving results and accurate enough to indicate concentrations of hydrogen sulfide ranging from those that are harmless or but slightly harmful to those immediately dangerous to life. It will indicate hydrogen sulfide in the range of 0.0025 to 0.05 per cent.

The complete detector (Fig. 86) consists of a small-inlet metal barrel corrugated on the end to permit a rubber tube to be attached, to which is attached a rubber aspirator bulb, a movable scale, and a tube containing the white granular reagent.

The reagent used in the hydrogen sulfide detector tubes consists of silver cyanide, $Ag(CN)_3$, on activated alumina, Al_2O_3.[28] The activated alumina serves as a carrier for the silver cyanide in a manner analogous to the pumice used in the hoolamite carbon monoxide tube, as explained on page 420. The chemical action which proceeds is given by the following reaction formula:

$$2AgCN + H_2S \longrightarrow Ag_2S + 2HCN$$

The reaction of the silver cyanide in the presence of hydrogen sulfide turns the white granules to a dark gray because of the formation of black silver sulfide. This begins at the end of the tube where the sample enters.

It should be noted that when the detector is used in the presence of hydrogen sulfide, hydrogen cyanide is liberated. This is an equally deadly gas. However, no anxiety should be felt regarding the use of the detector even in still air for the amount of hydrogen cyanide liberated is so small that the amount that can be formed by an entire tube is harmless even if the user inhaled the entire amount.

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[26] S. Roberts and G. Minors, *J. Soc. Chem. Ind.*, *53*, 526T (1934).

[27] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines*, *Miners' Circ. 33* (1938).

[28] J. B. Littlefield, W. P. Yant, and L. B. Berger, *U. S. Bur. Mines*, *Rept. Invest. 3276* (1935).

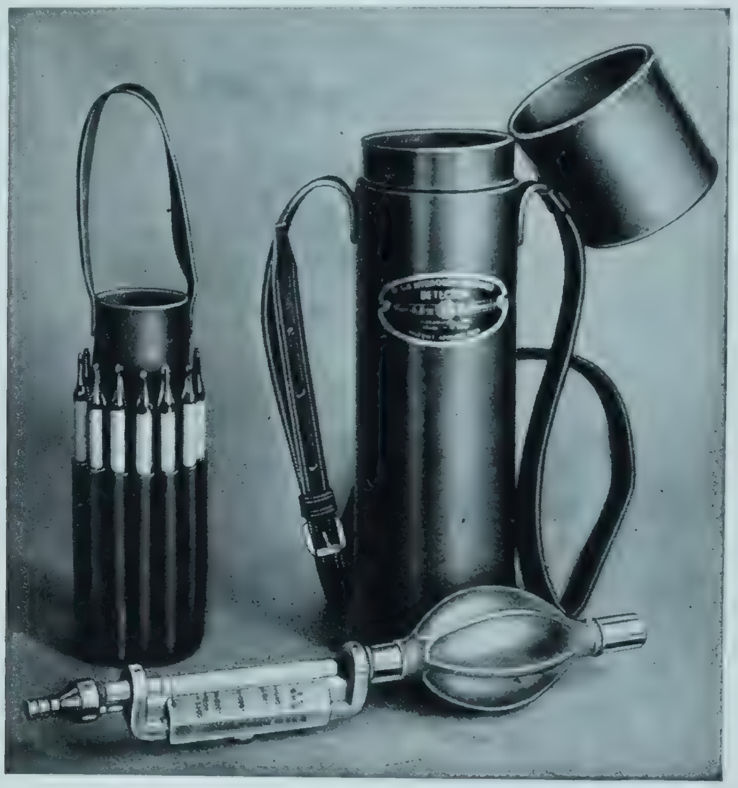

Fig. 86. Hydrogen sulfide detector. (*Courtesy Mine Safety Appliances Co.*)

Assuming that the person using the detector is protected by suitable respiratory apparatus when working in an atmosphere liable to contain hydrogen sulfide, the detector should be used as follows.

Break the tips of a detector tube (Fig. 87) and insert the red end—which is the end that should always be placed in the detector so that it will be nearest the aspirator bulb—through the tube guide at the top of the detector and place it in the opening directly above the aspirator bulb. Place the retaining head containing the inlet opening over the upper end of the detector tube. Slight pressure against the retaining head will insure a snug fit of the tube in the rubber seat. Loosen the thumb nut on the back of the detector and adjust the sliding scale until the zero is directly opposite the beginning of the chemical granules; then tighten the thumb nut and squeeze the aspirator bulb ten times, allowing it to expand completely each time. This will draw approximately 750 ml. of air through the chemical in the tube. Read the per cent of hydrogen sulfide on the scale midway between the longest and shortest ends of the gray discoloration of the detector tube. Temperature and storage have little effect on the tubes or the reaction. The commonly occurring gases do not interfere.

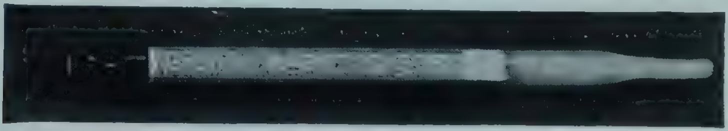

Fig. 87. Hydrogen sulfide detector tube.
(*Courtesy Mine Safety Appliances Co.*)

c. Determination

Cadmium Sulfide Method.[29] This method is based on the precipitation of cadmium sulfide in weakly acid or in ammoniacal solution from some cadmium salt by the hydrogen sulfide. The amount of the cadmium sulfide precipitate is then estimated iodometrically. The amount of hydrogen sulfide may then be ascertained by calculation.

Aspirate a known quantity of air at a known temperature and pressure through two bubblers in series containing water to which has been added 10 ml. of ammoniacal cadmium chloride solution, prepared by dissolving 20 g. of cadmium chloride in 400 ml. of water, adding 250 ml. of concentrated ammonia water, specific gravity 0.90, and then diluting the whole to 1 liter. After sampling has been completed and the sample has been removed to the place of analysis, remove any sulfur dioxide that may have been trapped along with the hydrogen sulfide by aspirating 10 liters of air through both absorbers. This air may be trapped in turn by one of the procedures described in the section on sulfur dioxide. If any considerable quantity of hydrogen sulfide is present, there will be a distinct yellow precipitate. Transfer the precipitate and solutions from the absorption tubes to a glass-stoppered bottle. Wash the absorbers and add the washings to the bottle. Dissolve the cadmium sulfide by the use of concentrated hydrochloric acid, washing out the absorbers first with the acid before transferring to the bottle. Add the acid slowly and with constant stirring until the solution is virtually colorless and acid to litmus. Titrate at once with 0.04 *N* iodine solution, using starch to indicate the end point. If desired, add an excess of iodine and back-titrate with standard thiosulfate solution.

The results of the analysis may be computed to hydrogen sulfide percentages by use of the formulas:

$$1 \text{ ml. } 0.001\ N\ I_2 \backsimeq 0.112 \text{ ml. of } H_2S \text{ at S.T.P.}$$

$$\%\ H_2S \text{ at S.T.P.} = \frac{\text{Vol. of sample at S.T.P.}}{\text{ml. } I_2 \text{ used} \times \text{value of 1 ml.}} \times 100$$

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[29] E. D. Gardner, S. P. Howell, and G. W. Jones, *U. S. Bur. Mines, Bull.* 287 (1927).

Other cadmium solutions, as, for instance, cadmium acetate,[30] may be used as the absorbing solution. The details of the method and the iodometric estimation are practically the same.

A modification of this method is the following.[31] Use an apparatus containing three absorbers in series. Each of the absorbers contains 100 ml. of cadmium chloride solution, 20 g. of cadmium chloride, $CdCl_2$, dissolved in 900 ml. of water to which is added 20 ml. of 0.5 N sodium hydroxide solution. Draw air through the train at the rate of 30 liters per hour for about 1 hour.

Transfer the contents of the first two absorbers to a glass-stoppered bottle. Use the contents of the third absorber if the concentration of hydrogen sulfide is high. Rinse the absorbers with water and then with concentrated hydrochloric acid, using 25 ml. of the acid for each 100 ml. of absorbing solution and rinse collected in the flask. Mix the combined absorbing solution, rinse water, and rinse acid. Rapidly add 25 ml. of 0.005 N iodine solution and titrate the excess iodine with 0.005 N sodium thiosulfate solution. Use starch solution as indicator near the end point. Continue the titration until no color remains in 5 ml. of chloroform when shaken with the solution titrated.

One ml. of 0.005 N iodine solution is equivalent to 0.0846 mg. of hydrogen sulfide. This quantity of hydrogen sulfide in 30 liters of air represents 2.0 parts of hydrogen sulfide per million of air at 25° C. and 1 atmosphere of pressure.

The method is accurate to about 0.5 part per million for a 30-liter air sample when testing air whose concentration of hydrogen sulfide is within the range of hygienic significance.

Iodine Method. In the absence of other oxidizing or reducing gases, hydrogen sulfide, as already mentioned, may be estimated iodometrically. The following procedure may be used as a field test. The method is accurate to about 95 per cent.

Procedure. Pass the air being tested through a midget impinger of the fritted disk type at a measured rate through 0.01 N iodine in potassium iodine solution until the mixture has been practically decolorized. The amount of hydrogen sulfide present can be calculated from the relationship that:

$$1 \text{ ml. of } 0.01\ N\ I_2 \approx 0.1223 \text{ ml. } H_2S \text{ at } 25° \text{ C. and } 760 \text{ mm.}$$

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[30] E. Quitmann, *Z. anal. Chem., 109,* 241 (1937).

[31] S. Moskowitz, J. Siegel, and W. J. Burke, *N. Y. State Ind. Bull. 19,* 33 (1940).

Hence:

$$\frac{\text{Ml. } 0.01\ N\ I_2 \times 0.1223 \times 1000}{\text{Min. sampling time} \times \text{sampling rate (l./min.)}} = \text{Ppm. } H_2S$$

Consequently where the rate is 1 liter per minute the equation reduces to:

$$\frac{\text{Ml. } 0.01\ N\ I_2 \times 122.3}{\text{Min. sampling time}} = \text{Ppm. } H_2S$$

It may also be estimated by trapping the gas in sulfate-free ammoniacal hydrogen peroxide.[32] The ammoniacal hydrogen peroxide oxidizes the hydrogen sulfide to sulfate:

$$H_2S + 4H_2O_2 \longrightarrow H_2SO_4 + 4H_2O$$

Three per cent sulfate-free hydrogen peroxide is prepared as directed on page 316. To 94 ml. of this solution add 6 ml. of 25 per cent ammonium hydroxide solution. Fifteen ml. of this ammoniacal hydrogen peroxide solution is placed in each absorber and the determination is then made as described for sulfur dioxide.

Nitroprusside Method.[33,34] The sodium nitroprusside test is not as sensitive nor as selective as either the lead acetate or the silver cyanide tests for hydrogen sulfide. Of the many variations of this method the following may be used.

Aspirate air through a gas-washing bottle containing 25 ml. of water to which has been added 2 ml. of 1 per cent sodium nitroprusside solution, 1 g. of $Na_2Fe(CN)_5NO.2H_2O$ dissolved in water and made up to 100 ml. and a few drops of ammonium chloride solution, until the solution becomes definitely colored. A control solution of 25 ml. of water and the same amounts of sodium nitroprusside and ammonium hydroxide is treated dropwise with a solution of arsenious sulfide with the aid of a microburette until the color intensity is the same as that of the unknown. The arsenious sulfide solution is prepared by dissolving 0.0367 g. of arsenious sulfide, As_2S_3, in a little ammonium hydroxide and diluting to 100 ml. One ml. of this solution is equivalent to 0.1 ml. or 0.143 mg. of hydrogen sulfide at 0° C. and 760 mm. of pressure. The hydrogen sulfide content may then be calculated according to the formula:

$$H_2S = \frac{0.143\ a}{M}$$

where:

a = ml. of As_2S_3 solution used
M = liters of air passed through the absorber

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[32] A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases,* Service to Industry, Hartford, 1936.

[33] K. A. Smirnov, *Zavodskaya Lab.,* 6, 240 (1937); *Chem. Abstracts,* 31, 6135 (1937).

[34] J. Bell and W. K. Hall, *Chemistry & Industry, 1936,* 89.

***p*-Aminodimethylaniline Sulfate Method.**[35-37] Hydrogen sulfide may be estimated colorimetrically with *p*-aminodimethylaniline sulfate in the presence of zinc and iron.

Procedure. Absorb the hydrogen sulfide in a gas-absorption bottle containing 130 ml. of 1 per cent zinc acetate solution and 5 ml. of 10 per cent sodium hydroxide solution. Disconnect the absorption bottle after sampling a known volume of air and add 25 ml. of diamine reagent, prepared by dissolving 0.1 g. of *p*-aminodimethylaniline sulfate in 100 ml. of hydrochloric acid (1:1). Mix this reagent and the test solution with any remaining zinc hydroxide by a rapid whirling of the bottle. Add 5 ml. of 0.02 M ferric chloride solution (0.02 M ferric chloride, $FeCl_3.6H_2O$, in 4 per cent hydrochloric acid) and mix. A blue color develops which is proportional, after a 2-hour reaction, to the amount of hydrogen sulfide present. Transfer the blue solution to a 250-ml. volumetric flask, and dilute to the mark.

When the hydrogen sulfide amounts to 0.1 mg. or more, a blue color, which can be matched very readily with standards after 2 hours, is obtained. Quantities of hydrogen sulfide of less than 0.1 mg. have a tendency to form a greenish tinge which predominates over the blue in solutions after standing overnight. As the standard colors are prepared in advance and are kept for several weeks, it is best to allow the test solutions of low hydrogen sulfide content to stand overnight before matching with the standards.

Preparation of Standards. The standards may be prepared by dissolving chemically pure sodium sulfide in water. Allow to stand for several hours, then estimate the sulfide content iodometrically. After the concentration is ascertained, dilute a portion with boiled and cooled water so that each ml. contains 0.1 mg. of sulfur. In preparing the standard colors, place 130 ml. of 1 per cent zinc acetate solution and 5 ml. of 10 per cent sodium hydroxide solution in a 250-ml. volumetric flask. Transfer the requisite amount of standard sodium sulfide solution with a pipette to the volumetric flask, followed immediately by 25 ml. of the diamine reagent and 5 ml. of 0.02 M ferric chloride solution. After the colors develop, dilute the solutions to the mark. The colors may be compared in a colorimeter or in Nessler tubes, but the standard used should not be over 100 per cent stronger than the test solution under analysis.

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[35] L. H. Almy, *J. Am. Chem. Soc., 47,* 1381 (1925).

[36] W. Mecklenburg and F. Rosenkranzer, *Z. anorg. Chem., 86,* 143 (1914).

[37] S. E. Sheppard and J. H. Hudson, *Ind. Eng. Chem., Anal. Ed., 2,* 73 (1930).

In place of sodium sulfide, which requires troublesome protection against oxidation, a solution of allylthiourea may be used. This must be checked by gravimetric determination as silver sulfide after treatment with ammoniacal silver chloride solution.

4. Carbon Disulfide

Carbon disulfide is a chemical compound which was and is widely used in industry. It was formerly used a great deal in the vulcanization of rubber. It finds use in the manufacture of artificial silk, of textiles, and as a solvent in industry. For instance, it is used to extract the remaining oil from olive marc. Such oil is known as sulfur oil. Carbon disulfide is also used as a disinfectant and fumigant. Dangerous concentrations may also be encountered in works in which coal gas, tar distillation products, and certain chemicals are manufactured.

Carbon disulfide is a colorless, volatile, highly combustible, generally foul-smelling liquid. It boils at 46° C.; has a specific gravity of 1.26; a refractive index of 1.629 at 18° C.; and a flash point below room temperature. Its lower inflammable limit is 1.25 per cent by volume in air and its upper limit is 50.0 per cent by volume. It ignites spontaneously between 125 and 135° C., so that even contact with a warm steam pipe or an electric light may be sufficient to cause ignition of the vapor. Its inflammability makes it an undesirable material to use in industry.

a. Physiological Response and Toxicity

Carbon disulfide, if inhaled in sufficient quantity, has a narcotic effect. The symptoms of chronic poisoning vary from slight fatigue and giddiness to serious mental derangement, nervous disorders, blindness, and paralysis. In high concentrations, carbon disulfide may cause delirium, coma, and death from respiratory failure.

The effects of the inhalation of various concentrations of carbon disulfide vapor in air may be summarized as follows: Repeated daily exposures to concentrations of the order of 0.1–0.2 mg. per liter, that is 33–66 parts per million, produce a general condition of ill-health with headache, drowsiness, and hysterical outbursts. An isolated exposure for a few hours to a concentration of 1 mg. per liter (333 parts per million) will produce severe headache and mental dullness or confusion. Repeated daily exposures to this concentration order result in increasingly severe symptoms with neuritis, distorted vision, and mental disturbance. Exposure to concentrations of the order of 6–10 mg. per liter (2,000–3,333 parts per million) for half an hour may result in serious illness and danger of mania and coma.[38] The toxic effects of low concentrations of carbon disulfide have been studied by Wiley, Kueper, and von Oettingen[38a] and experiences in using this material in industry have been reviewed by Barthelemy.[38b]

The accepted maximum safe permissible workroom concentration of carbon disulfide vapor in air is 20 parts per million, as indicated in Table 5, Appendix.

b. Detection and Determination

The methods used for the determination of the amount of carbon disulfide in air fall into two main groups. The first is the division in which the sulfur of the compound is oxidized to sulfate, which is subsequently detected and estimated gravimetrically. The second is the division in which the carbon disulfide is condensed with alkali and alcohol and is estimated as the resultant xanthate, or is condensed with diethylamine and a copper salt with the formation of diethyldithiocarbamate. The latter are simpler and more rapid methods. Matuszak[39] reviews some of the methods for the estimation of carbon disulfide.

Detection with Diethylamine and Copper Acetate. The British standard method[38] adopted for the detection of carbon disulfide in air depends upon its interaction with diethylamine and copper acetate, with the formation of a colored compound, copper diethyldithiocarbamate. Samples of air to be tested are drawn by means of a hand pump through a bubbler containing the reagents and the mixture is allowed to stand. The color developed is compared with a series of standards and from the number of pump strokes made and the color obtained, the concentration can be estimated by reference to a table. Concentrations down to 0.025 mg. per liter can be detected in this manner with 20 strokes, or less, of the pump.

Hydrogen sulfide will also produce a color with this reagent and therefore must be removed by filtering through lead acetate paper.

Apparatus. Sample the atmosphere by means of the hand pump described on page 33, using a nozzle to which a rubber tube can be attached. Draw the sample through the reagent contained in a bubbler consisting of a side-arm test tube of approximately 0.75-inch internal diameter and about 6 inches in length. Fit the tube with a rubber stopper through which passes a delivery tube about $^1/_8$-inch bore reaching nearly to the bottom of tube. The delivery tube must end in a fine jet. The opening of the jet can be adjusted by drawing out the tube and then inserting a gauge wire while the tube is in the flame. The nozzle can be cut at the point desired. A trap must be inserted in the line between the pump and the bubbler in order to prevent any of the reagent from being accidentally drawn into the pump. The apparatus may be mounted as shown in Figure 88, *B*.

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[38] *Dept. Sci. Ind. Research Brit., Leaflet 6* (1939).

[38a] F. W. Wiley, W. C. Kueper, and W. F. von Oettingen, *J. Ind. Hyg. Toxicol., 18,* 733 (1936).

[38b] N. L. Barthelemy, *J. Ind. Hyg. Toxicol., 21,* 141 (1939).

[39] M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed., 4,* 98 (1932).

Preparation of Reagent. Prepare the reagent by dissolving 2 ml. of diethylamine in 100 ml. of benzene. Warm 0.1 g. of copper acetate with a little absolute alcohol and make up to 100 ml. with absolute alcohol. To prepare the mixed reagent used for the test, transfer 10 ml. of absolute alcohol to the bubbler, add 2 ml. of diethylamine solution and 2 ml. of the copper acetate solution, and stir the mixture.

Preparation of Standards. Dissolve 1 ml. of reagent carbon disulfide in absolute alcohol in a 100-ml. volumetric flask and make up to volume with absolute alcohol. This is a 1 per cent volume solution. Transfer 1 ml. of this 1 per cent solution to a 50-ml. volumetric flask and make up to volume with absolute alcohol. This yields a 0.02 per cent volume solution.

Transfer the following volumes of 0.02 per cent carbon disulfide solution and make up to 10 ml. with absolute alcohol. Add 2 ml. of diethylamine reagent, 2 ml. of copper acetate solution, mix well, and allow to stand for 15 minutes for full development of color.

Standard	Volume of 0.02% CS_2 soln.
1	0.25 ml.
2	0.5 ml.
3	1.0 ml.
4	2.0 ml.

The standards must be prepared in tubes of the same bore as the bubbler. They should be prepared from the 0.02 per cent carbon disulfide solution immediately before the test or at least on the same day. If they are to be kept for some time they must be tightly stoppered and placed in the dark.

Procedure. Before carrying out any test, check the valves of the hand pump, with the bubbler disconnected, by closing the inlet with the finger and drawing out the piston slowly to its full length. On releasing the piston, it should rapidly return to its original position. The washer on the pump piston may shrink in the course of time. This may be remedied by soaking the piston in warm liquid paraffin for a few hours.

Place the reagent in the bubbler as described. If hydrogen sulfide is also present in the atmosphere, fix a dry lead acetate paper (Section A3b) in a paper holder (Fig. 13) in such a way that the atmosphere entering the solution passes through the lead acetate paper first. Draw 1, 2, 3, 5, or 20 strokes of the pump very slowly, 10 seconds per stroke, in the atmosphere to be tested. Remove the bubbler and allow to stand for 15 minutes. At the end of this period compare the color, if any is developed with the prepared standards, holding the test bubbler and the standard tubes side by side and observing by transmitted daylight.

The concentration of carbon disulfide, corresponding to the depth of color produced and the number of strokes, may be obtained from the following table:

Number of strokes	Standard			
	1	2	3	4
1	1/6,000	1/3,000	1/1,500	1/750
2	1/12,000	1/6,000	1/3,000	1/1,500
3	1/18,000	1/9,000	1/4,500	1/2,300
5	1/30,000	1/15,000	1/7,500	1/3,800
20	1/120,000	1/60,000	1/30,000	1/15,000

To sample and test in inaccessible places, use the methods suggested in Chapter II.

Modified Diethylamine Method.[40] Viles has modified the diethylamine method for the determination of carbon disulfide and has presented alternative methods for sampling.

Preparation of Reagent. Add to 1 liter of 85–100 per cent ethyl alcohol 1 ml. of diethylamine, 20 ml. of practical triethanolamine, and 0.05 g. of copper acetate. Mix thoroughly and allow to stand until all the copper acetate dissolves. If a turbidity develops, allow the mixture to stand 2 to 3 days to clear. This reagent, if kept well stoppered with a rubber stopper in a glass bottle, is stable. It contains sufficient reagent so that 10 ml. of the solution will completely absorb and react with a concentration of 120 parts per million of carbon disulfide in 1 liter of air.

Preparation of Standards. A stock standard alcohol solution may be prepared by dissolving a known weight of carbon disulfide in 100 ml. of alcohol. Because of the difficulty of accurately weighing out small amounts of carbon disulfide, it is better to prepare the standards from a saturated water solution. This is made by shaking excess liquid carbon disulfide with water in a glass-stoppered bottle. After the droplets of carbon disulfide have settled and the water layer is perfectly clear, pipette exactly 1 ml. of this solution into 50–75 ml. of alcohol in a 100-ml. volumetric flask. Make up to volume with alcohol and mix thoroughly.

The solubility of carbon disulfide in water is 0.22 g. per 100 ml. at 22° C. and 0.195 g. at 30° C. It may be assumed, then, that 0.2 g. of carbon disulfide per 100 ml. is the concentration of the water layer (26–30° C.). The resultant alcohol standard solution contains 0.00002 g., or 20 micrograms, of carbon disulfide per ml. Since 0.1 ml. can be accurately measured, it is possible to make up standards 2 micrograms apart. In a 322-ml. air volume sample this is equivalent to 2 parts per million of carbon disulfide.

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[40] F. J. Viles, *J. Ind. Hyg. Toxicol.*, *22*, 188 (1940).

Color standards can be made up in 4-microgram intervals for use in Nessler tubes. Standards ranging from 0–50 micrograms offer best comparisons. If a sample contains more carbon disulfide than the highest color standard, take an aliquot portion of the sample and make it up to 10 ml. with additional reagent and then compare with standards. By multiplying the number of micrograms found in the aliquot by the factor, 10/ml. of aliquot, the total number of micrograms of carbon disulfide in the sample may be calculated. The standards remain stable, if stoppered, for three days.

Interferences. Hydrogen sulfide interferes and is eliminated by absorption in sodium hydroxide solution in this modification. Dimethyl sulfide, thiophene, and mercaptans do not interfere.[41] Thioacetic acid gives reactions similar to carbon disulfide.

Procedure. Viles[40] uses four methods of sampling, as illustrated in Figure 88. The apparatus *A* is an adaptation of the U. S. Bureau of Mines apparatus for the determination of benzene (page 528). It consists of a bubbler unit, containing glass beads, which is connected to the air intake of an aspirator.

Place 2 to 3 ml. of the reagent in the trap. Allow water to flow out of the aspirator bottle and regulate the air flow so that a 250-ml. air sample is collected in 15–30 minutes. The volume of air sample is measured by the amount of water displaced.

Empty the contents of the bubbler trap into a beaker and wash the bubbler and the beads with two 3-ml. portions of the reagent. Transfer to a tall 50-ml. Nessler tube. Make up the volume to 10 ml. and allow to stand for 15 minutes for full development of the color. The test solution should be exposed as little as possible to the contaminated air to prevent any additional absorption of carbon disulfide vapor by the reagent.

A magnesium citrate bottle may be used for sampling by flushing with a rubber-bulb aspirator. Mercury may be used as an internal seal. The air sample is then displaced through the bubbler (as shown in Fig. 88, *C*) by water displacement. The analysis is then performed as above.

An evacuated tube of 325 ml. capacity may be used to take a sample. The contents are analyzed by setting the tube up vertically and adding 10 ml. of the reagent by means of a capillary tube through an open stopcock (Fig. 88, *D*). The stopcock is closed, the tube shaken for 0.5 to

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[41] N. Tischler, *Ind. Eng. Chem., Anal. Ed., 4,* 146 (1932).

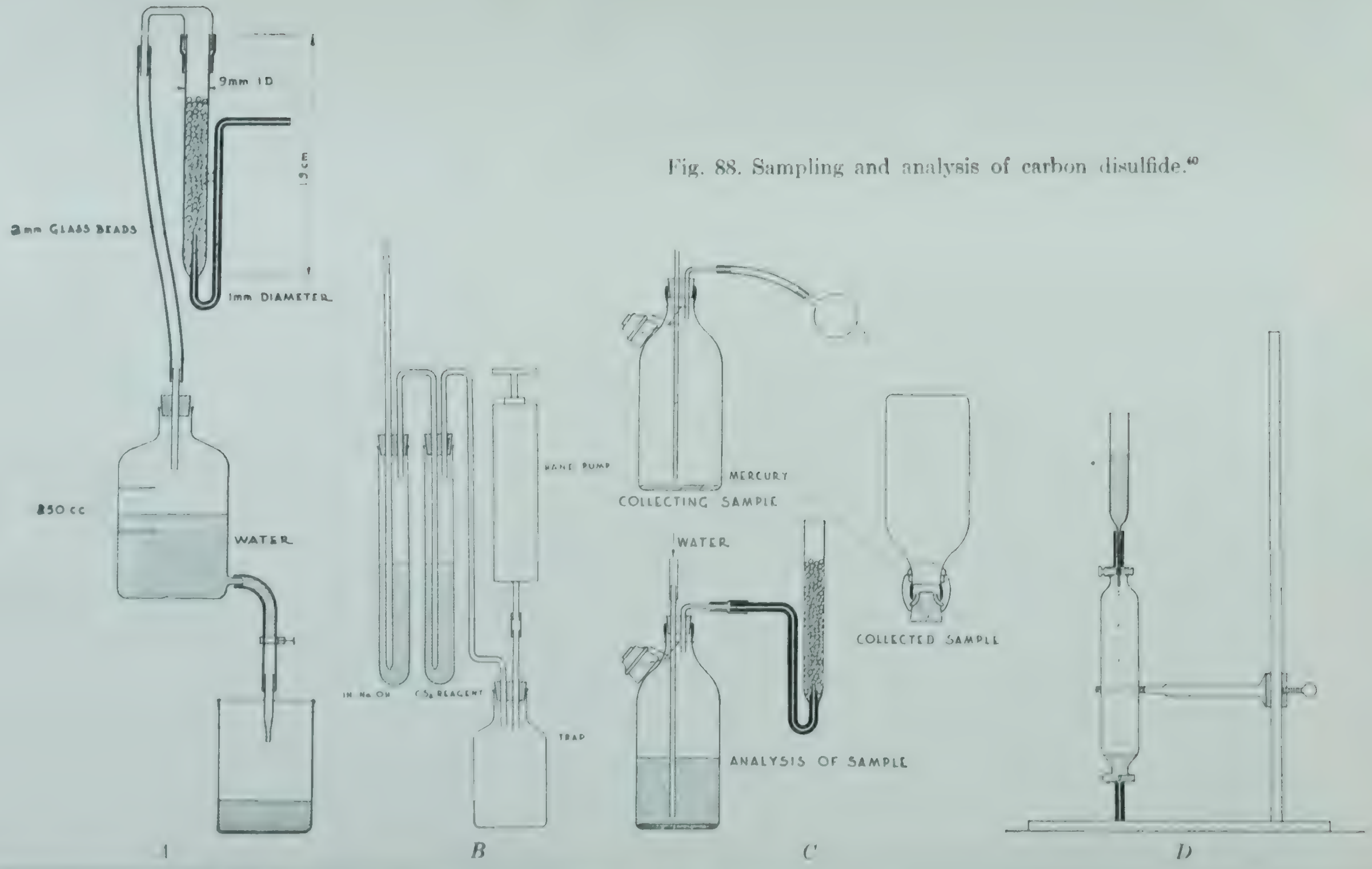

9mm ID
19cm
2mm GLASS BEADS
1mm DIAMETER
250 cc
WATER
A
1N NaOH
CS₂ REAGENT
HAND PUMP
TRAP
B
MERCURY
COLLECTING SAMPLE
WATER
ANALYSIS OF SAMPLE
COLLECTED SAMPLE
C
D

Fig. 88. Sampling and analysis of carbon disulfide.[60]

1 hour, and then the contents are transferred to the Nessler tube for comparison with standards.

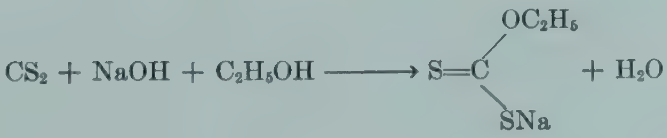
Viles also uses a hand-pump method, using sodium hydroxide solution to eliminate the interference of hydrogen sulfide (Fig. 88, *B*). Place 10 ml. of the reagent in the test tube nearest the sampling pump. Before attaching the pump, draw 2 strokes so that the pump is flushed with the atmosphere to be tested. For comparison, two standards are kept on the opposite side of the vertical support, one containing 22 micrograms and the other 45 micrograms of carbon disulfide. These standards must be kept stoppered to prevent additional absorption of carbon disulfide from the atmosphere.

Concentration of Carbon Disulfide by Diethylamine Method

Number of strokes, 60-ml.-capacity pump	Standard 1 22 γ, ppm.	Standard 2 45 γ, ppm.
1	120	240
2	60	120
3	40	80
4	30	60
6	20	40
8	15	30
12	10	20
24	5	10

Draw 6–9 strokes with the pump so that the air bubbles through the solution at a slow rate, 20–30 seconds for one pump stroke of 60 ml. capacity. Comparisons are made with the standards in order to estimate the concentration of carbon disulfide. Take a second sample so that it matches one of the standards closely. This may be difficult to obtain but between the two samples a fairly accurate estimate of the carbon disulfide concentration can be made. The concentration of the test atmosphere may be obtained from the table above. A sampling bubbler, using a rate of 60 ml. per minute, may also be employed.

Xanthate Method. This method depends upon the fact that when carbon disulfide is drawn through an alcoholic fixed alkali solution, an alkali xanthate is formed.



$$CS_2 + NaOH + C_2H_5OH \longrightarrow S{=}C\begin{matrix} OC_2H_5 \\ SNa \end{matrix} + H_2O$$

The xanthate so formed may be estimated as copper xanthate or iodometrically. It is essential for proper estimation that the alcoholic potash or soda used to absorb and react with the carbon disulfide be fresh, that the formation of any appreciable proportion of free xanthic acid be avoided, and that the iodine titration, if one is made, be made as soon as possible after the formation of the xanthate.

After passing the air through one or more absorbers, depending on the type governing the completeness of absorption, containing a 5 per cent solution of alkali in ethyl alcohol, transfer the specimen so obtained to a glass-stoppered bottle or flask. Acidify the solution with *N* acetic acid, using phenolphthalein and litmus papers as outside indicators, until the solution is acid to phenolphthalein but alkaline to litmus. Add starch indicator solution and titrate immediately with 0.006862 *N* iodine solution.

$$2S{:}COC_2H_5.SK + I_2 \longrightarrow 2KI + (S{:}COC_2H_5.S)_2$$

With iodine solution of the normality stated, each mg. of carbon disulfide requires about 2 ml. of the iodine solution. For less than mg. amounts, a more dilute solution of iodine should be used.

Alternatively the xanthate may be estimated by adding it slowly with constant stirring to a sufficiently acid mixture of standard iodate containing excess iodide. These reagents will react to liberate iodine, which may then be determined by the usual thiosulfate titration. The exact amount of xanthate, hence of carbon disulfide, can be calculated from the relationship that

$$1 \text{ mol } CS_2 \Bumpeq 1 \text{ mol } S{:}COC_2H_5SK \Bumpeq 1 \text{ mol } I_2$$

By boiling the alcoholic alkali solution with hydrogen peroxide, the xanthate may be oxidized to sulfate, which is ascertained by precipitation as the barium salt.

The xanthate may be precipitated by the addition of copper sulfate solution[42] or by a solution of copper acetate in acetic acid. The cuprous xanthate formed is filtered off, washed, and dissolved in a minimum amount of nitric acid. From this point the copper may be determined iodometrically as described under the estimation of copper (page 286). The copper xanthate may be redissolved after filtration in very dilute nitric acid and may then be estimated colorimetrically as detailed under the xanthate method for copper (page 287).

Colorimetric Xanthate Method.[43] Draw air through a train of two absorbers containing 100 ml. each of 0.1 *N* potassium hydroxide in absolute ethyl alcohol, at a rate of 30 liters per hour for about 1 hour.

Make up the contents of the two absorbers to 100 ml. with alcohol, if necessary. Withdraw a 40-ml. aliquot from each and place in separate 50-ml. Nessler tubes. Add to each tube 2 drops of phenolphthalein indicator solution, sufficient acetic acid to make the mixture faintly acid, and 4 drops of 0.5 per cent cupric acetate solution. Mix the contents of the tubes and make up to 50-ml. volume with alcohol. Simultaneously prepare a series of standards by adding from 0.1 ml. to 1.0 ml. of a solution of carbon disulfide in alcohol, containing 0.25 mg. of carbon disulfide per ml., to 40 ml. of 0.1 *N* alcoholic potassium hydroxide. Treat each of these tubes similarly with acetic acid and cupric acetate solution. Compare the yellow color of copper ethyl xanthate of the test solutions with the standards having the closest match in color intensity. A colorimeter may be used if available.

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[42] W. J. Huff, *J. Am. Chem. Soc.*, *48*, 81 (1926).

[43] S. Moskowitz, J. Siegel, and W. J. Burke, *N. Y. State Ind. Bull. 19*, 33 (1940).

One mg. of carbon disulfide is equivalent to 10.6 parts of carbon disulfide per million of air if 30 liters of air were sampled. The accuracy of the absorption and estimation is within 0.5 part per million if 30 liters of air containing a concentration of carbon disulfide of hygienic significance is sampled.

5. *Mixed Volatile Sulfur Compounds*

In many industries volatile sulfur compounds occur together and it is often important to allot to each its proper role as a hazard. For instance, in the manufacture of sulfuric acid by the chamber process sulfur dioxide, sulfur trioxide, and hydrogen sulfide may occur together, not to speak of water vapor, nitric oxide, nitrogen tetroxide, and oxygen. In the artificial-silk industry methyl mercaptan, carbon disulfide, and hydrogen sulfide may happen to be together, as may carbon disulfide and hydrogen sulfide, or carbon disulfide, hydrogen sulfide, and sulfur dioxide. In blasting operations hydrogen sulfide and sulfur dioxide, if formed, are almost always produced together.

a. Hydrogen Sulfide and Sulfur Dioxide

A prior section (page 316) has dealt with the estimation of sulfur trioxide and sulfur dioxide. Methods for the estimation of sulfur dioxide and hydrogen sulfide in the presence of one another have been indicated, on page 316, by a combination of the sulfur dioxide-hydrogen peroxide method and one of the other methods for sulfur dioxide, and on page 323 by the ammoniacal cadmium acetate-hydrogen sulfide method.

Hydrogen sulfide and sulfur dioxide are not compatible in large amounts for they react as follows:

$$SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$$

In limited quantities they do exist together for a short time.

Another method[44,45] is based on the different rates of oxidation of sulfur dioxide and hydrogen sulfide in air with atmospheric oxygen in an ammonium hydroxide solution. The sulfate produced is precipitated with lead nitrate. A known volume of air is passed through an absorber containing 0.2 per cent ammonium hydroxide solution at a temperature of 50° C. The solution is shaken for 30 minutes. It is then evaporated to half its volume with the addition of water and 1 drop of nitric acid. The residue is dissolved in dilute alcohol and is made up to a definite volume. An aliquot part is treated directly with lead nitrate to determine sulfur dioxide sulfate. Another aliquot is first oxidized with hydrogen peroxide and is then treated with lead nitrate to determine hydrogen sulfide sulfate.

Another method is to trap the air in four absorbers, the first two contain 5 per cent potassium chlorate solution and the second two contain an ammoniacal solution of hydrogen peroxide. The sulfur dioxide is completely oxidized to sulfur trioxide by the potassium chlorate, while only 1–2 per cent of the hydrogen sulfide is oxidized. The remaining hydrogen sulfide is oxidized by the ammoniacal hydrogen peroxide. The sulfate produced in the absorbers is determined and the amount of each gas may then be calculated.

b. Carbon Disulfide and Hydrogen Sulfide[46-48]

Carbon disulfide and hydrogen sulfide often exist together during the production of artificial silk by the process that uses carbon disulfide. In the presence of carbon disulfide, the odor of hydrogen sulfide is changed and it requires 0.9 mg. per cubic meter instead of about 0.6 mg. per cubic meter to detect hydrogen sulfide by smell. To estimate these gases in the presence of one another, pass air through five absorbers in series, the first three containing 100 ml. each of cadmium chloride solution, 20 g. of cadmium chloride, $CdCl_2$, dissolved in 900 ml. of water to which is added 20 ml. of 0.5 N sodium hydroxide solution. The last two bubblers contain 100 ml. each of 0.1 N potassium hydroxide in absolute ethyl alcohol.

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[44] V. G. Gurevich and V. P. Vendt, *J. Gen. Chem. U.S.S.R.*, *6*, 962 (1936); *Chem. Abstracts*, *31*, 629 (1937).

[45] V. G. Gurevich. *J. Russ. Phys.-Chem. Soc.*, *62*, 111 (1930); *Chem. Abstracts*, *2* 5254 (1930).

[46] S. Moskowitz, J. Siegel, and W. J. Burke, *N. Y. State Ind. Bull. 19*, 33 (1940).

[47] H. L. Barthelmy, *Am. Pub. Health Assoc. Yearbook*, *1936–37*, 93; *J. Ind. H* *Toxicol.*, *21*, 141 (1939).

[48] H. Frauenhof, *Kunstseide*, *17*, 344 (1935).

Draw air through the train at the rate of 30 liters per hour for about 1 hour. At the end of the sampling time, draw uncontaminated air through the train for another 5 minutes to prevent any possible entrainment of carbon disulfide in the first three absorbers.

The hydrogen sulfide is trapped in the first absorbers as cadmium sulfide. The carbon disulfide is trapped in the alcoholic potash. The amount of hydrogen sulfide caught in the first three bubblers may be estimated iodometrically, as detailed on page 324, and the carbon disulfide in the last two absorbers may be estimated by one of the methods detailed for carbon disulfide such as the colorimetric ethyl xanthate method described on page 333.

c. Hydrogen Sulfide, Sulfur Dioxide, and Carbon Disulfide[49]

These gases may be estimated in the presence of one another by adsorbing the gases in a series of tubes on different adsorbents. The gases are then liberated individually, reduced, if necessary, to hydrogen sulfide, and estimated iodometrically.

The hydrogen sulfide is trapped by asbestos impregnated with silver chloride. The adsorbent is prepared by the action of hydrochloric acid on silver oxide, freshly precipitated on asbestos. The sulfur dioxide is adsorbed on a porous refractory impregnated with manganese dioxide. This adsorbent is prepared by precipitation from potassium permanganate by alcohol. The carbon disulfide is adsorbed on porous stone impregnated with an alcoholic solution of sodium hydroxide. Each adsorbing tube is heated in turn in a current of hydrogen containing a little hydrochloric acid. The carbon disulfide and sulfur dioxide are thus reduced to hydrogen sulfide. The hydrogen sulfide may then be caught by one of the methods previously detailed and estimated iodometrically or by some other method if preferred.

d. Hydrogen Sulfide, Carbon Disulfide, and Methyl Mercaptan[50]

The air in the spinning rooms of rayon factories may sometimes contain hydrogen sulfide, carbon disulfide, and methyl mercaptan together. These gases may be separated by means of solid lead acetate. Draw the air containing the gases through a series of four wash bottles. The first two are Jena wash bottles with No. 83 G1 glass filters or equivalent devices and contain 20 ml. of 0.5 *N* sodium hydroxide solution. The next two are very small bubblers with gas dispersers and each contains 2 ml. of sodium hydroxide in ethyl alcohol. After sampling is complete, unite the contents of the first two wash bottles, add 4 ml. of 25 per cent hydrochloric acid, and connect immediately to an apparatus for detecting mercaptan and sulfide. This apparatus consists of two tubes (20 by 9 cm.) connected with a ground joint. The first tube contains calcium chloride and the second tube contains about 20 g. of fine lead acetate. This second tube is connected with a small wash bottle containing 1 ml. of isatin-sulfuric acid solution, 10 mg. of isatin dissolved in 100 ml. of sulfuric acid and freshly prepared for use. Draw air slowly through the apparatus for 30 minutes. The hydrogen sulfide is absorbed by the lead salt and the mercaptan colors the isatin reagent a grass green. By the depth of this color the quantity of mercaptan can be estimated colorimetrically within the range of 0.005–0.1 mg. with an accuracy of about 0.01 mg. The hydrogen sulfide may be estimated from the depth of color produced in the lead acetate or it may be liberated and estimated as previously described.

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[49] J. Böeseken and H. D. Muller, *Rec. trav. chim., 50,* 1117 (1931).

[50] J F. Reith, *Rec. trav. chim., 53,* 18 (1934).

Pour the contents of wash bottles 3 and 4 of the first absorption apparatus into a beaker and rinse out the wash bottles first with 2.5 ml. of 4 *N* acetic acid, then with 10 ml. of cupric acetate solution, 0.92 mg. of cupric acetate in 250 ml. of solution. After at least 2 hours, filter off the copper xanthate precipitate in a three G4 glass filtering crucible and wash with not over 25 ml. of water. The formation of the yellow precipitate is proof of the presence of carbon disulfide. The quantity may be calculated by determining its copper content iodometrically by one of the methods previously detailed, or as follows.

Place the crucible on a 25-ml. suction flask and add 0.5 ml. of 4 *N* acetic acid and 4 drops of fresh saturated aqueous bromine to the precipitate. Cover with a watch glass. After 5 minutes connect with suction, add 4 drops more of bromine water, and filter after 5 minutes. This serves to dissolve the yellow precipitate. Wash the filter until the total volume of the filtrate is 10 ml. and mix with 0.5 ml. of 5 per cent phenol solution to remove the excess bromine. After 5 minutes add 2.5 ml. of *N* potassium iodide solution and titrate the liberated iodine with 0.01 *N* sodium thiosulfate solution, 1 ml. of which is equivalent to 1.52 mg. of carbon disulfide.

6. Sulfur Monochloride

Sulfur monochloride, S_2Cl_2, sulfur chloride, is a reddish-yellow liquid, which boils at 138° C. and has a specific gravity of 1.678. It is decomposed by water with the formation of sulfur dioxide, sulfur, and hydrochloric acid. It is soluble in carbon disulfide, ether, benzene, and other organic solvents. It is a solvent for sulfur and fats.

Sulfur monochloride is used in the vulcanization of rubber; in the formulation of printing inks, varnishes, and cements; as a solvent for sulfur, oils, and fats; in the hardening of soft woods; and as an insecticide. It is also used in the chlorination of organic compounds—for instance, in the manufacture of mustard gas.

Sulfur monochloride has a suffocating, nauseating, and pungent odor. It induces lachrymation and is an irritant for the mucous membranes of the nose, throat, and especially the eyes. The compound is highly toxic but because it readily decomposes, as mentioned above, into sulfur dioxide and hydrochloric acid, it may also cause injury because of the presence of these compounds. Since it is often used in combination with other substances such as benzene and carbon disulfide, the hazard resulting from the other components of the mixture may be greater than that attributable to the sulfur monochloride when it is present in low concentration. The recommended maximum allowable concentration is 1 part per million parts of air.

It may be estimated by slowly passing a measured volume of contaminated air through a silver nitrate solution acidified with nitric acid.[51] The precipitated silver chloride may be redissolved in ammonia and then reprecipitated with nitric acid. An alternative procedure is to pass the air through a fritted bubbler containing N sodium hydroxide solution. Chloride may then be estimated by customary methods.

Sulfur chloride may be estimated titrimetrically. Absorb the material in 0.1 N silver nitrate solution acidified with nitric acid as mentioned. Add a known volume of 0.1 N sodium chloride solution equivalent to the volume of silver nitrate used. Titrate the excess chloride ion with 0.1 N silver nitrate solution. Calculate the sulfur chloride from the relationship that:

$$2S_2Cl_2 + 2H_2O + 4AgNO_3 \longrightarrow 4AgCl + 3S + SO_2 + 4HNO_3$$

7. *Thionyl Chloride*

Thionyl chloride, sulfurous oxychloride, $SOCl_2$, is used industrially in the preparation of chlorinated substances, among which may be mentioned the preparation of mustard gas. It is a colorless, strongly refractive liquid, which fumes on contact with air and has a suffocating odor. It boils at 78–79° C., has a specific gravity of 1.638, and a refractive index of 1.527 at 10° C. It recomposes rapidly in water with the formation of hydrochloric acid and sulfur dioxide. It is soluble in benzene and chloroform but decomposes in acid, alkali, and alcohol.

It is an eye irritant and because of its decomposition into hydrochloric acid and sulfur dioxide exerts the harmful effects of those substances on the human body. Patty[51a] suggests a maximum permissible workroom limit of less than 5 parts per million.

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[51] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

It may be estimated in a manner similar to that described for sulfur monochloride or by other methods applicable to the determination of chloride ions, as described in Chapter X.

8. Sulfuryl Chloride

Sulfuryl chloride, sulfuryl oxychloride, SO_2Cl_2, is used in the preparation of chlorosulfonates—for instance, methyl and ethyl chlorosulfonates. During World War I, it was used in combination with phosgene, chloropicrin, and cyanogen chloride to make the toxic gases visible. It was also used as a smoke agent.

Sulfuryl chloride is a colorless liquid with a pungent odor. It boils at 69° C., has a specific gravity of 1.667, and a refractive index of 1.444 at 20° C. It is decomposed by water with the formation of sulfuric acid and hydrochloric acid, the reaction being very rapid with warm water. It is soluble in acetic acid and benzene and in the war gases mentioned above. Its ability to be used as a smoke depends on its hydrolysis by the water vapor of the air.

Its physiological effect is due no doubt to its hydrolytic products and so it has an irritating effect. The maximum permissible workroom concentration should probably be of the same order as that of thionyl chloride.

It may be estimated by the methods used for the determination of either sulfate or chloride as described in the respective section covering those analytical methods.

9. Carbon Oxysulfide

Carbon oxysulfide, carbonyl sulfide, COS, is a colorless gas with practically no odor when pure. It boils at —48° C. and weighs 2.72 g. per liter. It forms an explosive mixture with air. It is decomposed by water and bases with the formation of carbon dioxide and hydrogen sulfide.

It is only slightly irritating and works principally on the central nervous system. A concentration of 400 parts per million could be borne by mice for 15 minutes; however, a concentration of 3,200 parts of carbon oxysulfide per million parts of air caused serious illness in rabbits after exposures of 60 minutes and a concentration of 0.6 per cent by volume or 6,000 parts per million caused death after an exposure of 50 minutes.

[51a] F. A. Patty, ed., *Industrial Hygiene and Toxicology* (Vol. II), Interscience, New York, 1949.

The concentration of carbon oxysulfide can be determined by slowly passing the air containing the gas through a tube having an electrically heated platinum spiral. The gas is decomposed to sulfur and carbon monoxide. The sulfur is oxidized to sulfur dioxide which may subsequently be estimated by absorption by caustic potash.

Preferably pass the gas into a solution of alcoholic potash, in which it decomposes with the formation of potassium carbonate and potassium sulfide, and subsequently estimate the sulfide.

10. Sulfides and Thiols

Several sulfides and thiols (mercaptans), other than those mentioned in previous sections, may be industrially hazardous. Thus, for instance, in the onion-dehydrating industry, onion oil, which consists largely of sulfide components of the type of allyl disulfide and allyl propyl disulfide, has irritating properties.[52] Xylyl mercaptan is another compound that has been mentioned as a possible industrial hazard.

Allyl sulfide, $(CH_2{:}CHCH_2)S_2$, diallyl disulfide, so-called garlic oil, is a colorless liquid with a garlic-like odor. It boils at about 139° C. and has a specific gravity of 0.888. It is miscible with alcohol and is insoluble in water. *Allyl propyl disulfide,* $CH_2{:}CHCH_2SSCH_2CH_2CH_3$, has analogous properties.

Combustion methods[53] similar to those described for the determination of halogenated hydrocarbons (see page 570) may be used for the estimation of such volatile sulfides and thiols. The sulfur is oxidized to sulfur dioxide, which is absorbed, converted to sulfite, oxidized to sulfate, and estimated titrimetrically.

Procedure. Draw air through the combustion apparatus at a rate of 1 liter per minute at 900° C. Trap the gases evolved in a gas absorber containing glass beads wetted with 2 per cent sodium carbonate solution. Transfer the samples to 125-ml. flasks. Add 5 ml. of saturated bromine water to oxidize all the sulfite to sulfate, make the sample just acid to hydrochloric acid, and heat to drive all the excess bromine. Proceed with the titrimetric tetrahydroxyquinone method described on page 311.

The titrimetric method may be used advantageously for total concentrations of sulfur in the air sample of the order of 100 mg. at least.

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[52] B. Feiner, W. J. Burke, and J. Baliff, *J. Ind. Hyg. Toxicol., 28,* 278 (1946).
[53] B. Feiner, W. J. Burke, and S. Moskowitz, *J, Ind. Hyg. Toxicol., 28,* 276 (1946).

For lower concentrations it is preferable to use standard nephelometric and turbidimetric procedures.

11. Allyl Isothiocyanate

Allyl isothiocyanate, $CH:CHCH_2NCS$, allyl isosulfocyanate, or allyl mustard oil, also called at times artificial oil of mustard and volatile oil of mustard is a colorless to pale-yellow liquid with a very irritating, pungent odor and an acrid taste. The U. S. P. product is the oil obtained by maceration with water and subsequent distillation of the dried ripe seed, free from fixed oil, of *Brassica nigra* (Linné) Koch or of *Brassica juncea* (Linné) Czerniaew, or prepared synthetically. It has a specific gravity of 1.013–1.020 at 25° C., boils at 150.1° C., and has a refractive index of 1.5275–1.5310 at 20° C. It is miscible with alcohol, ether, and carbon disulfide, and 0.2 g. dissolves in 100 ml. of water. Allyl isothiocyanate is used in pharmaceutical preparations for external application which cause redness of the skin and in synthetic spice flavorings.

Allyl isothiocyanate reacts with silver nitrate in ammoniacal solution with the quantitative precipitation of silver sulfide:

$$C_3H_5NCS + NH_3 \longrightarrow C_3H_5NHCSNH_2 \text{ (thiosinamine)}$$

$$C_3H_5NHCSNH_2 + 2Ag^+ + 2NH_3 \longrightarrow \underset{\text{(allyl cyanamide)}}{C_3H_5NHCN} + Ag_2S + 2NH_4^+$$

Procedure. Trap the allyl isothiocyanate in alcohol. Transfer an aliquot of the alcoholic solution to a 100-ml. volumetric flask. Add 50 ml. of 0.1 or 0.01 *N* silver nitrate solution and 5 ml. of 10 per cent ammonium hydroxide solution. Connect the flask to a reflux condenser and heat on a water bath for 1 hour. Cool, disconnect, make up to 100 ml., mix thoroughly, and filter through a dry filter. Reject the first 10 ml. Transfer 50 ml. of the filtrate to a flask, add 5 ml. of nitric acid, add 2 ml. of 0.5 *N* ferric ammonium sulfate solution, and titrate the excess silver nitrate with 0.1 or 0.01 *N* ammonium thiocyanate solution. A blank test should be made using an equivalent amount of alcohol, and then subtract the blank from the result obtained in the titration. Each milliliter of 0.1 *N* silver nitrate solution is equivalent to 0.004958 g. of allyl isothiocyanate.

12. Thiocyanates

While few texts on toxicology mention poisoning attributable to thiocyanates, it is known that toxic symptoms occur when thiocyanates are used in the treatment of hypertension. A case of alleged poisoning attributable to potassium thicyanate was noted in 1945.

Pyrazolone Method. Based on the reactions discussed on page 451, thiocyanate ion can be estimated.[54] The reagents used are detailed as noted.

Add 0.2 ml. of 0.1 per cent ferric chloride solution and 0.2 ml. of 1 per cent chloramine T solution to 1 ml. of a solution containing up to 2.5 micrograms of thiocyanate ion. Stopper the tube and shake. After 3 minutes of contact time, add 6 ml. of the pyridine-pyrazolone mixture. Stopper the tube again and mix. After 20 minutes, take readings in a spectrophotometer set at 630 mμ with the optical density of the reagent blank set at zero. The color is stable for at least 30 minutes at room temperature.

B. PHOSPHORUS

The part that phosphorus has played as an industrial hazard is historic. This was undoubtedly due to the notoriety given the cases of industrial poisoning attributable to phosphorus or its compounds as well as to the horrible appearance that the unfortunate victims of this industrial disease assumed. "Phossy jaw" was as much in the public eye not so many years ago as "silicosis" is now.

It was in the manufacture of lucifer matches, matches made with white, that is, yellow, phosphorus, that these cases first arose. It took more than 50 years to begin to regulate the use of white phosphorus and it was not until the relatively nonpoisonous phosphorus sesquisulfide match was developed that really stringent regulations could be drawn and enforced against the use of white phosphorus as such in matches. Phosphorus sesquisulfide may cause dermatitis in workers allergic to it.

White phosphorus is still a hazard in industry, particularly among workers in fireworks, fertilizers, insecticides, rat pastes, phosphorus-extracting plants, brass founders, bone-black makers, substitutes for camphor in celluloid, and in general where phosphorus compounds are used in quantity, including match workers.[55] The toxicology of chronic phosphorus poisoning has been reviewed in detail by Heimann.[56] The maximum allowable concentration of yellow (white) phosphorus is 0.1 mg. per cubic meter of air.

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[54] J. Epstein, *Anal. Chem., 19,* 272 (1947).

[55] E. F. Ward, *U. S. Bur. Labor Statistics, Bull.* 405 (1926); *J. Ind. Hyg., 10.* 314 (1928).

[56] H. Heimann, *N. Y. State Ind. Bull. 26,* No. 4, 17 (1947); *26,* No. 5, 22 (1947).

Special mention should be made of phosphine, phosphoreted hydrogen. This gas is highly poisonous and is closely related to arsine. It is generated in industry under circumstances closely analogous to the generation of arsine.

1. Sampling

Phosphate-bearing dust and phosphorus fumes can be sampled by many of the methods detailed before. The acid fumes may be caught by means of fixed alkali solution. The dusts may be trapped in water, by electrical precipitation, or by filtration. In the latter two methods, after making the cellulosic materials alkaline, the specimen may be ashed, either by the wet method or by ignition. Phosphorus is usually determined and estimated as phosphoric acid expressed as P_2O_5. This may be done gravimetrically as magnesium pyrophosphate, $Mg_2P_2O_7$, or titrimetrically, or colorimetrically. In general the ash is dissolved in sulfuric acid or in nitric acid or in both, or the wet ash is used, and a suitable aliquot is taken for the analysis. Phosphorus may also be sampled as detailed below for phosphine.

2. Determination

a. Gravimetric Method

In this method the phosphate is first precipitated as ammonium molybdiphosphate, which is dissolved in ammonium hydroxide and then is reprecipitated as magnesium ammonium phosphate. This precipitate is then converted to the pyrophosphate by ignition. This method is used for larger quantities of phosphorus.

Reagents. (a) Molybdate Solution.—Dissolve 100 g. of molybdic acid, MoO_3, in a mixture of 144 ml. of ammonium hydroxide and 271 ml. of water. Pour this solution slowly and with constant stirring into a mixture of 489 ml. of nitric acid and 1,148 ml. of water. Keep the final mixture in a warm place for several days or until a portion of the reagent heated to 40° C. deposits no yellow precipitate of ammonium molybdiphosphate. Decant the solution from any sediment and preserve in glass-stoppered bottles.

(b) Magnesia Mixture.—Dissolve 11 g. of magnesium oxide in hydrochloric acid (1:4), avoiding an excess of the acid; add a little magnesium oxide in excess; boil a few minutes to precipitate iron, aluminum, and phosphorus pentoxide, and filter. To the filtrate add 140 g. of ammonium chloride and 130.5 ml. of ammonium hydroxide and dilute to 1 liter. Or dissolve 55 g. of magnesium chloride, $MgCl_2.6H_2O$, in water, add 140 g. of ammonium chloride, and dilute to 870 ml. Add ammonium hydroxide to each required portion of the solution just before using, in the proportion of 15 ml. to 100 ml. of solution.

(c) Magnesium Nitrate Solution.—Dissolve 150 g. of magnesium oxide in nitric acid (1:1), avoiding an excess of the acid; add a little magnesium oxide in excess, boil, filter from the excess of magnesium oxide, ferric oxide, etc., and dilute to 1 liter.

Determination. Transfer the solution containing the ash or other solution containing the phosphate to a 250-ml. beaker; add ammonium hydroxide in slight excess and barely dissolve the precipitate formed with a few drops of nitric acid, stirring vigorously. If hydrochloric acid or sulfuric acid had been used as a solvent, add about 15 g. of crystalline ammonium nitrate or a solution containing that quantity. To the hot solution add 70 ml. of the molybdate solution for every decigram of phosphorus pentoxide present. Digest at about 65° C. for 1 hour, and determine whether or not the phosphorus pentoxide has been completely precipitated by adding more molybdate solution to the clear supernatant liquid. Filter, and wash with cold water or preferably with a solution of 100 g. of ammonium nitrate dissolved in and diluted to 1 liter of water. Dissolve the precipitate on the filter with ammonium hydroxide solution (1:1) and hot water and wash into a beaker to a volume of not more than 100 ml. Neutralize with hydrochloric acid, using litmus paper or bromothymol blue as indicator; cool; and from a burette add slowly, at about 1 drop per second, stirring vigorously, 15 ml. of the magnesia mixture for each decigram of phosphorus pentoxide present. After 15 minutes add 12 ml. of ammonium hydroxide. Let stand until the supernatant liquid is clear (about 2 hours), filter, wash the precipitate with ammonium hydroxide (1:9) until the washings are practically free of chlorides, dry, burn at a low heat, and then ignite in an electric furnace at 950–1000° C., cool in a desiccator, and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. Calculate the result as precentage of phosphorus pentoxide.

b. Titrimetric Method

Add 5–10 ml. of nitric acid, depending on the manner of solution, or add the equivalent in ammonium nitrate. Add ammonium hydroxide until the precipitate that forms dissolves but slowly on stirring vigorously, dilute to 75–100 ml., and adjust to a temperature of 25–30° C. Add sufficient molybdate solution to insure complete precipitation. Five ml. of nitric acid must be added to every 100 ml. of molybdate solution, which is then filtered immediately before use. Place the solution in a shaking machine or stirring apparatus and shake for 30 minutes at room temperature. Decant at once through a filter and wash the precipitate twice by decantation with 25–30 ml. portions of water, agitating thoroughly and allowing to settle. Transfer the precipitate to the filter and wash with cold water until the filtrate from two fillings of the filter yields a pink color upon the addition of phenolphthalein and 1 drop of the standard alkali. The standard alkali is prepared by diluting 328.81 ml. of *N* alkali to 1 liter. One ml. of this solution is equivalent to 1 mg. of phosphorus pentoxide. Transfer the precipitate and filter to the beaker or precipitating vessel, dissolve the precipitate in a small excess of the standard alkali, add a few drops of phenolphthalein indicator, and titrate with standard acid. The standard acid is prepared to be equal to or one-half of the normality of the standard alkali solution.

c. Colorimetric Method

Truog Modification.[57] *Reagents.* Ammonium Molybdate Solution.—Dissolve 25 g. of ammonium molybdate in 200 ml. of water heated to 60° C., and filter. Cool and dilute with water to 1 liter. This solution then contains 2.5 g. of ammonium molybdate per 100 ml.

Sulfuric Acid Solution.—Dilute 280 ml. of arsenic- and phosphorus-free sulfuric acid to 1 liter with water. This is approximately a 10 N sulfuric acid solution.

Stannous Chloride Solution.—Place 25 g. of stannous chloride, $SnCl_2.H_2O$, in a solution of 100 ml. of hydrochloric acid diluted to 500 ml. with water. Let stand in a warm room until dissolved; then dilute to 1 liter with water. Filter if necessary. This reagent may be stored in a bottle with a side opening near the bottom and equipped with a stopcock for delivering the solution in drops. The solution may be protected from the air by floating a layer of white mineral oil about 5 mm. thick on the surface.

Standard Phosphate Solution.—Dissolve 0.2195 g. of recrystallized potassium dihydrogen phosphate, KH_2PO_4, in water and dilute to 1 liter. This solution contains 50 parts of phosphorus per million of solution and is too concentrated to use directly. A second stock solution may be made by taking 50 ml. of the first stock solution and diluting to 500 ml. The standard solution for color comparison is made by diluting 5 ml. of the second stock solution to 91 ml. with water; 4 ml. each of the ammonium molybdate solution and sulfuric acid solution are added and mixed thoroughly by swirling in a 150-ml. flask. Six drops of the stannous chloride solution are added and the solution is shaken again. The solution is diluted to 100 ml. and again mixed by swirling in the flask. The standard phosphate solution is ready for use but it is necessary to add a drop of stannous chloride solution every 10–12 minutes to obtain the full color. One ml. of this standard phosphate solution contains 0.00025 mg. of phosphorus per ml.

Determination. Dissolve the ash in 1 ml. of 10 N sulfuric acid. Add sufficient water to insure complete solution and transfer to a small beaker. If the specimen is in solution, evaporate to a small volume, add the same amount of acid, and transfer, if desired, to a small beaker. Neutralize with ammonia water using phenolphthalein as indicator. Transfer to a 100-ml. volumetric flask and make to volume.

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[57] E. Truog and A. H. Meyer, *Ind. Eng. Chem., Anal. Ed.*, *1*, 136 (1929).

Transfer by means of a pipette an appropriate aliquot to a 100-ml. volumetric flask with a mark at 91 ml., and dilute to that volume with water. Add 4 ml. each of the ammonium molybdate and 10 *N* sulfuric acid solutions, swirling after each addition. Add 6 drops of stannous chloride solution, shake, and make up to volume. Compare in a colorimeter within 10 minutes with a standard prepared as directed above. Comparison may also be made in Nessler tubes by using varying proportions of the standard phosphorus solution. Computation of the amount of phosphorus present may be made by use of the relationship that 1 ml. of the final prepared standard phosphate solution contains 0.00025 mg. phosphorus per ml.

Microcolorimetric Method. Phosphorus in the form of phosphate reacts with ammonium molybdate to form a complex molybdiphosphate. This complex is reduced to form a molybdenum blue by the use of solutions of hydroquinone and sodium sulfite.[58,59]

Reagents. Ammonium Molybdate Solution.—Dissolve 25 g. of ammonium molybdate in 300 ml. of water. Dilute 75 ml. of concentrated sulfuric acid to 200 ml. with water and add to the ammonium molybdate solution.

Hydroquinone Solution.—Dissolve 0.5 g. of hydroquinone in 100 ml. of water and add 1 drop of sulfuric acid to retard oxidation.

Sodium Sulfite Solution. Dissolve 200 g. of sodium sulfite, Na_2SO_3, in water, make up to 1 liter, and filter. Keep this solution well stoppered or prepare a fresh equivalent each time it is to be used.

Standards. Potassium Dihydrogen Phosphate Solution.—Dissolve 0.4394 g. of pure, dry potassium dihydrogen phosphate, KH_2PO_4, in water and make up to 1 liter. Dilute 50 ml. of this solution to 200 ml. Each ml. of the latter solution is equivalent to 0.05 mg. of phosphorus.

Procedure. Convert the phosphorus and phosphorus compounds to phosphate as detailed above. Transfer to a volumetric flask and make to volume. Transfer a 5-ml. aliquot to a 10-ml. volumetric flask. Add 1 ml. of the ammonium molybdate solution, rotate the flask to mix, and allow to stand a few moments. Add one ml. of the hydroquinone solution, again rotate the flask; add 1 ml. of the sodium sulfite solution and mix.

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[58] A. P. Briggs, *J. Biol. Chem.*, *69*, 255 (1924).

[59] *Methods Assoc. Official Agr. Chem.* (4th ed.), 1935.

Make to volume with water. Stopper the flask and shake thoroughly Allow to stand 30 minutes for development of the blue color and compare immediately thereafter in a colorimeter with 2 ml. of the standard potassium dihydrogen phosphate solution treated at the same time with the same reagents as the test solution and in the same way. With either the test solution or the standard set at 25.0 mm., readings within 10 mm., that is, with a range of 20 mm., are accurate. If concentrations of the test solution are outside this range, larger or smaller aliquots of the sample solution should be used.

3. Phosphine

Phosphine is an industrial hazard in a number of industries, among which may be mentioned the manufacture of acetylene, where calcium phosphide is an impurity in the calcium carbide, phosphorus extraction, the manufacture of phosphorus sesquisulfide, and operations with phosphorus-bearing ferrosilicon.

Phosphine, PH_3, is a colorless gas of nauseating odor. It acts on the central nervous system and the blood.[51] The symptoms exhibited by phosphine poisoning are an oppressed feeling in the chest, headache, vertigo, general debility, loss of appetite, and great thirst. A concentration of 2.8 mg. per liter, equivalent to 2,000 parts per million, is lethal to men in a few minutes. Concentrations of 0.56–0.84 mg. per liter, that is, 400 to 600 parts per million, are dangerous to life after exposures for 30 to 60 minutes. The maximum concentration tolerated for exposures of 60 minutes is in the range 0.14–0.26 mg. per liter, or 100–190 parts per million. The maximum concentration that can be tolerated without symptoms for several hours is 0.01 mg. per liter, or 7 parts per million.[60] The minimum warning concentration is 0.002–0.004 mg. per liter, that is, 1.4–2.8 parts per million. The maximum allowable concentration[61] is considered to be of the same order as arsine, namely, 0.05 part per million.

Detection and Determination

Phosphine may be detected by the brown to black color imparted to filter paper wet with silver nitrate solution by this substance. It may be estimated by trapping the gas in bromine water or sodium hypochloride solution in a fritted bubbler and after the elimination of the bromine, determination as phosphate as detailed above.

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[60] R. R. Sayers, in *International Critical Tables* (Vol. II), McGraw-Hill, New York, 1927.

[61] *Ind. Hyg. Newsletter, 7,* No. 8, 15 (1947).

Phosphine may be determined rapidly in gases by use of the reaction

$$PH_3 + 3HgCl_2 \longrightarrow P(HgCl)_3 + 3HCl$$

In this reaction, the quantity of acid liberated is proportional to the volume of phosphine present. A 100-ml. sample of the gas is measured into a flask over water. An open tube containing an excess of solid mercuric chloride is introduced into the flask and the mixture is shaken. The precipitate is filtered off and washed. The combined filtrate and washings are titrated with sodium hydroxide using methyl orange as indicator. The number of ml. of 0.1 N alkali multiplied by 0.784 gives the volume of phosphine at 15° C. and 760 mm. of pressure. For percentages below 0.5 per cent, a colorimetric determination may be made by suspending the $P(HgCl)_3$ precipitate, whose color varies from yellow to brown. This color is matched against a freshly prepared standard obtained with a gaseous mixture of known phosphine content.[62]

Phosphine, and phosphorus as well, may be sampled by drawing the air to be analyzed through three scrubbers in series each of which contains 10 ml. of 0.01 N potassium permanganate solution and 1 ml. of 5 per cent sulfuric acid to convert the phosphorus to phosphoric acid.[62a] The absorbing solution may then be combined, the excess permanganate is decolorized by heating with 0.01 N oxalic acid and the colorimetric procedures detailed above applied.

4. Phosphorus Trichloride

Phosphorus trichloride is used in the manufacture of phosphorus oxychloride, phosphorus pentachloride, and as a chlorinating agent for the manufacture of chlorinated organic compounds. It is used as a solvent for phosphorus.

Phosphorus trichloride, PCl_3, is a colorless liquid with a sharp smell and it fumes on exposure to air because of decomposition to phosphorous acid and hydrochloric acid. It boils at 76° C. and has a specific gravity of 1.574 at 21/4° C. It dissolves in water with the formation of the aforementioned compounds. It is also decomposed by alcohol. It is soluble in benzene, chloroform, ether, and carbon disulfide.

It enters the body as a vapor through the respiratory tract, which it attacks. It causes a sensation of suffocation, difficulty in breathing, lachrymation, bronchitis, edema, and inflammation of the lungs with frothy blood-stained expectoration. A concentration of 600 parts per million is lethal in a few minutes. Concentrations of 50 to 80 parts per million are harmful after exposures of 30 to 60 minutes. Two to 4 parts per million can be borne for exposures of 60 minutes without serious symptoms. A concentration of 0.7 part per million is the maximum that can be tolerated for exposures of several hours.[60] The maximum allowable concentration is considered to be 0.5 part per million.[61]

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[62] M. Wilmet, *Compt. rend., 185,* 206 (1927); *Analyst, 52,* 558 (1927).

[62a] W. Muller, *Arch. Hyg. Bact., 129,* 286 (1943).

It may be estimated by trapping in 20 per cent sodium hydroxide solution with subsequent determination of the liberated chloride.

Phosphorus pentachloride, PCl_5, and phosphorus oxychloride, $POCl_3$, which are also poisonous and have similar physiological effects, may be estimated in an analogous manner. The maximum allowable concentration for phosphorus pentachloride is 1 mg. per cubic meter of air.[61]

5. *Phosphorus Pentasulfide*

Phosphorus pentasulfide is used in the manufacture of safety matches, for the introduction of sulfur into organic compounds, and for the manufacture of ignition materials. Phosphorus pentasulfide, P_2S_5, also known as phosphoric sulfide and phosphorus persulfide, occurs in light-yellow crystalline masses, which have a peculiar odor. It melts at about 280° C. and boils at 523° C. in an inert atmosphere. It is soluble in carbon disulfide and in aqueous alkali solutions.

The maximum allowable concentration recommended for this compound is 1 mg. of phosphorus pentasulfide per cubic meter of air.

Phosphorus pentasulfide decomposes in water, forming hydrogen sulfide and phosphoric acid. Methods for the determination of these substances have been previously detailed.

C. NITROGEN

1. *Nitrogen Oxides*

Industrial poisoning from the oxygen compounds of nitrogen is a hazard in many industries. Among the industries where this hazard is particularly present may be mentioned the manufacture of sulfuric acid by the chamber process, which was discussed in a prior section; the manufacture of nitric acid and nitrates such as ammonium nitrate; the manufacture of dyes and explosives; the production of pyroxylin-type plastics; the formulation of nitrocellulose paints, lacquers, and artificial cloths; the manufacture of fertilizer and cyanamide; and photographic-film works. These gases are also a hazard in certain operations, among which may be mentioned blasting, welding, electroplating, metal cleaning, and in fires. In the Cleveland Hospital fire, in which many lives were lost, the lethal agent was mainly nitrogen oxides from burning film.[63] Nitrogen oxides are also produced in carbon-arc combustions. The concentration of these oxides expressed as nitric oxide varies from 200–1500 ppm., depending on the type of arc and the power consumption.[64]

a. Physiological Response

The fumes of the nitrogen oxides are extremely dangerous because of their insidious character. The bad feature of this type of poisoning is that little warning is given to the worker, for the oxides of nitrogen fail to set up defense respiratory reflexes. Thus a worker may inhale quantities of these gases that will affect him seriously and even cause death, without knowing it. Cases have been recorded where the workman felt entirely well throughout the working day after the inhalation of these fumes, only to die the following day because of pulmonary edema. Symptoms after exposure are restlessness, with a dry cough and shortness of breath. These symptoms increase and are accompanied by a frothy sputum tinged with blood. Death may follow from pulmonary edema, even after several days.

As little as 0.01 per cent (100 parts per million) may cause illness if breathed for a short time and 0.07 per cent, or 700 parts per million, is fatal if breathed for 30 minutes or even a lesser time.[65,66] The maximum concentration allowable for an exposure of several hours' duration is of the order of 10 parts per million.[67] The generally accepted maximum allowable concentration[68] for daily 8-hour exposures is 25 parts of nitrogen oxides, other than nitrous oxide, per million parts of air. When the nitrogen oxides are calculated as NO_2, this concentration is equivalent to 0.047 mg. per liter at 25° C. and 760 mm.

b. Chemical Relationship of the Nitrogen Oxides

Nitrogen forms a series of oxides, most of which may occur in industry. They are:

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[63] J. C. Olsen, A. S. Brunjes, and V. J. Sabetta, *Ind. Eng. Chem., 22,* 860 (1930).
[64] Coltman, *J. Ind. Hyg. Toxicol., 20,* 289 (1938).
[65] E. D. Gardner, S. P. Howell, and G. W. Jones, *U. S. Bur. Mines, Bull. 287* (1927).
[66] *Fed. Bd. Vocational Education, Bull. 39* (1931).
[67] *Dept. Sci. Ind. Research Brit., Leaflet 5* (1939).
[68] *Am. Standards* Z37.13–1944.

Nitrous oxide, N_2O	Anhydride of hyponitrous acid, $H_2N_2O_2$
Nitric oxide, NO	Anhydride of nitrohydroxylamic acid, $HON:NO_2H$
Nitrous anhydride, or nitrogen trioxide, N_2O_3	Anhydride of nitrous acid, HNO_2
Nitrogen tetroxide, or dioxide, $NO_2 \rightleftarrows N_2O_4$	Yields both nitrous and nitric acids
Nitric anhydride, or nitrogen pentoxide, N_2O_5	Anhydride of nitric acid, HNO_3

Only the first four are gases, and of these only the NO_2 form of nitrogen tetroxide is colored the familiar brown-red, the other gases, including the N_2O_4 form of nitrogen tetroxide, being colorless or practically colorless. There is another oxide of nitrogen, namely, nitrogen hexoxide, NO_3 or N_2O_6, about which little is known and which in all probability is seldom encountered in industry.

The relationships of nitric oxide, NO; nitrous anhydride, N_2O_3; and nitrogen tetroxide, N_2O_4 are so very close that they seldom occur separately in industry. Thus nitric oxide reacts readily with oxygen to form nitrogen tetroxide:

$$2NO + O_2 \rightleftharpoons \underset{\text{brown}}{2NO_2} \rightleftharpoons \underset{\text{faint yellow}}{N_2O_4}$$

Nitrous anhydride in the gaseous state is almost completely dissociated into nitric oxide and nitrogen tetroxide:

$$N_2O_3 \longrightarrow NO + NO_2$$

Nitrogen tetroxide dissolves in *cold* water to form both nitric and nitrous acids:

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

If the water is not cold, the nitrous acid decomposes to form nitric acid and nitric oxide:

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Nitrogen pentoxide, or nitric anhydride, is a white solid that has to be prepared by special methods. It decomposes readily, forming nitrogen tetroxide:

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

c. Detection and Determination

Because of these relationships and reactions, the mixture of nitric oxide, nitrous anhydride, and nitrogen tetroxide, which appears as reddish brown fumes, is preferably estimated as nitrate.[69] In the specific instance of arc welding, the nitric oxide, NO, constant is probably only one-fifth of the total calculated as nitrate.

Samples of nitrogen oxides may be taken in special glass vacuum-tube collectors of approximately 250- to 300-ml. capacity. These tubes should be rinsed with water several times before the absorbing solution is added, to free the tubes of nitrogen oxides that may have collected on the walls during their manufacture. The tubes are prepared beforehand as follows: Place 10 ml. of 0.1 N sulfuric acid and 3 drops of a 3 per cent solution of hydrogen peroxide into the bottle through the 6-mm. shell-tubing neck on each bottle. Connect the tube to a high-vacuum pump and evacuate until the solution in the collector begins to boil. Seal the tube with an alcohol hand torch. Make a file mark on the neck of the collector near the end and break the tube at this point in the place where the sample is to be collected. After the tip is broken the surrounding air rushes in until it reaches the pressure of the surrounding atmosphere. The tips of the collectors may then be sealed with a rubber policeman or with a short piece of pure gum-rubber tubing having a stub of solid glass rod in the end.

Sampling of the oxides of nitrogen may also be accomplished by absorption of the fumes in sodium hydroxide solution, oxidation with hydrogen peroxide to insure that all of the oxides are in the nitrate form, and subsequent determination of the nitrate by the phenoldisulfonic acid method.

An alternative method of sampling is to pass 10 liters of the air to be sampled by aspiration over a period of 1 hour through 40 ml. of absorbing solution consisting of 35 ml. of 5 per cent potassium hydroxide solution and 5 ml. of 3 per cent hydrogen peroxide solution.[70] This absorbing solution is then analyzed by the phenoldisulfonic acid method.

Immerse the samples obtained as described above in a brine bath and freeze the absorbing solution.[71] Keep the samples in the low-temperature bath for at least 2 hours to insure complete oxidation of the oxides. After the gases are completely oxidized, wash the outside of each tube thoroughly and dry. Then open the tube and wash the contents into a 150-ml. beaker. Make slightly alkaline with N sodium hydroxide solution, cover the beaker with a watch glass supported on glass hooks, and evaporate nearly to dryness on an electric hot plate. To prevent baking, drive off the last traces of moisture by placing the beaker in a constant-temperature oven thermostatically controlled at 85° C. As soon as dryness is attained, cool the beaker in a cold water bath and proceed with the method as detailed below, beginning with "Add 1 ml. of the phenoldisulfonic acid solution—."

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[69] C. P. McCord, G. C. Harrold, and S. F. Meek, *J. Ind. Hyg. Toxicol.*, *23*, 200 (1941).

[70] E. L. MacQuiddy, J. P. Tollman, L. W. La Towsky, and M. Mayliss, *J. Ind. Hyg. Toxicol.*, *20*, 312 (1938).

[71] G. St. J. Perrott, L. W. Babcock, C. D. Bitting, and G. W. Jones, *U. S. Bur. Mines, Tech. Paper 482* (1930).

Phenoldisulfonic Acid Method.[72–74] The following method is based on the nitration of phenoldisulfonic acid by any nitrate present in the sample with the formation of a colored nitrophenoldisulfonic acid compound. Any nitrite present is oxidized to nitrate and thus reacts the same way.

Reagents. (a) Phenoldisulfonic Acid Solution.—Dissolve 25 g. of pure phenol in 150 ml. of concentrated sulfuric acid on a steam bath, cool, and add 75 ml. of fuming sulfuric acid (15 per cent SO_3). Heat to 100° C. for 2 hours. Do not expose to light.

(b) Standard Comparison Solution.—Stock Nitrate Solution.—Dissolve 0.4025 g. of recrystallized and dried potassium nitrate in water and dilute to 1 liter.

(c) Standard Nitrate Solution.—Dilute 10 ml. of the stock nitrate solution to 1 liter with water. One ml. of this solution is equivalent to 0.001 ml. of nitrogen dioxide at 25° C., and 740 mm. Transfer aliquot portions to 150-ml. beakers, thus 1 ml. of standard nitrate solution would be equivalent to 5 parts per million on the basis of a 200-ml. sample. Add 10 ml. of 0.1 N sulfuric acid, 3 drops of hydrogen peroxide, and sufficient N potassium hydroxide solution to make the mixture alkaline. Dilute to 110 ml., evaporate to dryness, and proceed with the method as detailed.

Procedure. Transfer the sample solution to a beaker. Heat, if not collected by the vacuum-tube method, for a few minutes with a few drops of nitrate-free hydrogen peroxide, or oxidize any nitrite present with dilute potassium permanganate solution, adding the permanganate until a faint pink coloration persists. Evaporate. Transfer to a 100-ml. volumetric flask. If the chloride content exceeds 3 mg., add to the cold solution sufficient silver sulfate solution, prepared by dissolving 4.397 g. of Ag_2SO_4, nitrate-free, in 1 liter of water (1 ml. of this solution is equivalent to 1 mg. of chloride ion) to precipitate all but about 0.1

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[72] R. L. Beatty, L. B. Berger, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3687* (1943).

[73] J. Piccard, E. G. Peterson, C. D. Bitting, *Ind. Eng. Chem., Anal. Ed.*, **2**, 3 (1930).

[74] G. C. Harrold, S. F. Meek, and C. P. McCord, *J. Ind. Hyg. Toxicol.*, **22**, 347 (1940).

mg. of chloride. Add 5 ml. of alumina cream. Make up to the mark with water, shake thoroughly, and filter through a folded filter, returning the filtrate to the filter until it runs through clear. Evaporate 25 ml. or other suitable aliquot of the filtrate to dryness.

Add 1 ml. of the phenoldisulfonic acid solution. Mix quickly and thoroughly by means of a glass rod. Add 1 ml. of water and 3–4 drops of sulfuric acid. Heat on a steam bath for 2–3 minutes, being careful not to char the material. Then add about 25 ml. of water and an excess of ammonium hydroxide (1:1), about 20 ml., transfer to a 100-ml. volumetric flask, add 1 to 2 ml. of alumina cream if not perfectly clear, dilute to volume with water, and filter. Fill a 50-ml. Nessler tube to the mark with the filtrate and determine the quantity of sodium nitrate present in the sample by comparison with the standard comparison tubes prepared as directed above. If the solution is too dark for comparison with the standards, dilute with water and correct the result accordingly.

Nitrite by the Griess-Ilosvay Reaction. The nitrite present in the absorbing solution may be estimated by using it to diazotize some added sulfanilic acid. In this instance, of course, hydrogen peroxide must not be used. The diazotized sulfanilic acid is then coupled with α-naphthylamine hydrochloride. The official British[75] test is performed by passing the gas or atmosphere to be tested directly through the Griess-Ilosvay reagent.

Reagents. (a) Sulfanilic Acid Solution.—Dissolve 1 g. of sulfanilic acid in hot water, cool, and dilute to 100 ml.

(b) α-Naphthylamine Hydrochloride Solution.—Boil 0.5 g. of the salt with 100 ml. of water, kept at constant volume for 10 minutes.

(c) Standard Nitrite Solution.—Dissolve 1.1 g. of silver nitrite in nitrite-free water, precipitate the silver with sodium chloride solution, dilute to 1 liter, mix, allow to settle. Dilute 100 ml. of the supernatant liquid to 1 liter and then 10 ml. of this solution to 1 liter, using in each case nitrite-free water. One ml. of the final dilution is equivalent to 0.0001 mg. of nitrogen as nitrite.

Procedure.[76–78] Transfer the solution containing the nitrite to a suitable volumetric flask. Almost neutralize with sulfuric acid. Add 5 ml. of alumina cream and swirl. Make to volume with water, mix, and filter. These steps may be omitted if a clear test solution is used. Place 100 ml.

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[75] *Dept. Sci. Ind. Research Brit., Leaflet 5* (1939).

[76] *Methods Assoc. Official Agr. Chem.* (4th ed.), 1935.

[77] *Standard Methods of Water Analysis* (8th ed.), Am. Pub. Health Assoc., 1936.

[78] Weston, *J. Am. Chem. Soc., 27,* 281 (1905).

of the suitable aliquot in a 100-ml. Nessler tube and treat with 1 or 2 drops of hydrochloric acid. Add 1 ml. of the sulfanilic acid solution, 1 ml. of the α-naphthylamine hydrochloride solution, and mix thoroughly. Set aside for 30 minutes with other Nessler tubes containing known quantities of the standard nitrite solution made up to 100 ml. with nitrite-free water and treated with hydrochloric acid, sulfanilic acid, and the α-naphthylamine hydrochloride solutions in the same manner as the sample. Determine the quantity of the nitrite by comparison with the depth of pink color in the known and unknown solutions. If the color of the sample is deeper than that of the highest standard, repeat the test on a diluted sample.

Permanent standards may be prepared by matching the nitrite standards with dilutions of a solution of fuchsin, 0.1 g. of basic fuchsin in 1 liter of water.

Because of the instability of the α-naphthylamine complex, Germuth[79] recommends that dimethyl-α-naphthylamine, $C_{10}H_7N:(CH_3)_2$, be substituted for the α-naphthylamine. A solution of 5.25 g. of dimethyl-α-naphthylamine dissolved in 1 liter of 4 *N* acetic acid in 95 per cent methanol insures the most satisfactory results in the colorimetric estimation of nitrites. Such a solution is stable and is used in exactly the same manner as the α-naphthylamine hydrochloride as directed above. However, the method using *N*-(1-naphthyl)-ethylenediamine, detailed below, is to be preferred.

British Modification.[75] It is well to note that although the official British test is termed the detection of "nitrous fumes," it actually only detects the vapors of nitrous acid and its anhydride, nitrogen trioxide, N_2O_3. For the distinction between these terms see page 352.

The hand pump apparatus used in this test is described on page 33 and in the section on carbon disulfide, page 329.

Reagents. Sulfanilic Acid.—Dissolve 0.5 g. of sulfanilic acid with slight warming in 150 ml. of a solution of 70 ml. of glacial acetic acid in 500 ml. of water.

α-Naphthylamine.—Boil 0.1 g. of α-naphthylamine for a few minutes with 20 ml of water and pour the mixture into 150 ml. of a solution of 70 ml. of glacial acetic acid in 500 ml. of water.

Immediately before the test is made, place 5 ml. of each of these reagent solutions in the bubbler trap and mix.

Preparation of Standard Color.—Solution A.—Weigh accurately 0.1 g. of dimethylaminazobenzene, dissolve in acetone, and make up the solution to 100 ml. with acetone in a volumetric flask.

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[79] F. G. Germuth, *Ind. Eng. Chem., Anal. Ed., 1,* 28 (1929).

Solution B.—Pipette 5 ml. of Solution A into a 250-ml. volumetric flask and make to volume with acetone. Keep well stoppered and in the dark.

When required prepare the standard color from solution B as follows: Transfer 1 ml. of solution B by means of a pipette to a tube of equal bore as that of the test bubbler. Make up the volume to 10 ml. with 7 per cent hydrochloric acid. Keep the standard well stoppered or sealed and in the dark when not in use.

Procedure. On entering the atmosphere to be tested, draw the pumping strokes very slowly, using approximately 10 seconds per stroke. Continue pumping, counting the number of strokes made, until the depth of color developed is a little weaker than that of the standard color. Remove the test bubbler and after 2 minutes, to allow for the full development of color, compare with the standard tube, the two tubes being observed side by side by transversely transmitted daylight.

If the depth of color is the same in both tubes, the concentration of nitrite present is obtained from the table given below. If the test color is less than the standard, replace the test bubbler and draw further strokes of the pump until exact equivalence is reached on standing 2 minutes. If the test color is deeper, repeat the test with fresh reagent, using fewer strokes.

Concentration	No. of strokes
Above 1/8,000	less than 1
1/8,000–1/13,000	1–2
1/13,000–1/20,000	2
1/20,000–1/27,000	3
1/27,000–1/35,000	4
1/35,000–1/45,000	5
1/45,000–1/55,000	6
1/55,000–1/65,000	7
1/65,000–1/75,000	8
1/75,000–1/85,000	9
1/85,000–1/100,000	10

Under certain conditions a cloudiness may be produced in the test solution. This does not interfere with the comparison with the standard color.

Naphthylethylenediamine Method. Jacobs and Brodey[80] devised a rapid method by which nitrogen dioxide-nitrogen tetroxide may be detected and estimated within the atmosphere in which firemen and others are working. In this method, the Bratton and Marshall[81] reagents and a modification of the Patty and Petty[82,83] apparatus are employed. Per manent color standards have been developed for use with the Patty and Petty method.

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[80] Morris B. Jacobs and M. Brodey, paper presented at meeting, *Metropolitan N. Y. Section, Am. Ind. Hyg. Assoc.* (May, 1945).

[81] A. C. Bratton and E. K. Marshall, *J. Biol. Chem., 128,* 437 (1939).

[82] F. A. Patty and G. M. Petty, *J. Ind. Hyg. Toxicol., 25,* 361 (1943).

[83] P. R. Averell, W. F. Hart, N. T. Woodbury, and W. R. Bradley, *Anal. Chem., 19,* 1040 (1947).

Marshall and his co-workers,[81,84] in a method for the determination of sulfanilamide, that is, *p*-aminobenzenesulfonamide, and its analogues, proposed the replacement of *a*-naphthylamine by *N*-(1-naphthyl)-ethylenediamine dihydrochloride. Shinn[85] adopted this method for the determination of nitrite.

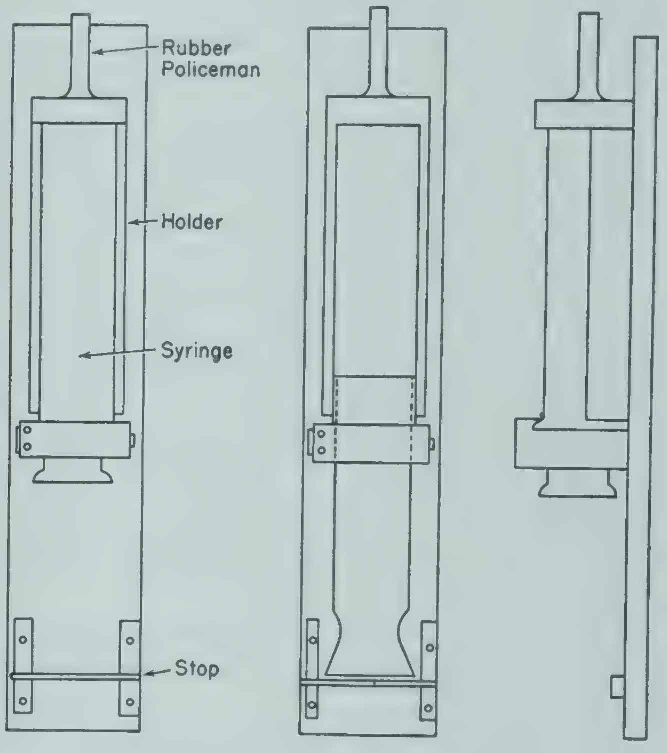

Fig. 89. 50-ml. syringe and holder.

Apparatus. The apparatus is a simple standard 50-ml. glass syringe which is placed in a holder (as shown in Fig. 89) so that it can be operated in the dark. By removing the rubber retaining "policeman," the plunger of the syringe falls to the stop, drawing in 50 ml. of air.

Reagents. Nitrite Reagent Powder.—Because of the necessity of having a reagent ready for use at moment's notice and the well-known instability of most of the liquid nitrite reagents commonly used, a powder reagent was prepared. This reagent has the following composition:

N-(1-naphthyl)-ethylenediamine dihydrochloride (coupling reagent)......	1.0 g.
Sulfanilamide (*p*-aminobenzenesulfonamide)	4.0 g.

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[84] E. K. Marshall and J. T. Litchfield, *Science, 88*, 85 (1938).
[85] M. B. Shinn, *Ind. Eng. Chem., Anal. Ed., 13*, 33 (1941).

Tartaric acid	95.0 g.
Total	100.0 g.

The substance should be in a fine powder and should be mixed dry.

Reagent powders containing 100 mg. of the mixed powder may be weighed out in papers and stored. Each powder is thus equivalent to 1 mg. of coupling reagent, 4 mg. of sulfanilamide, and 95 mg. of acid. The powders are stable for more than 1 year if kept dry and in the dark.

Reagent Solution.—Dissolve 1 powder in 10 ml. of water. This is sufficient for one test. This solution is relatively stable. Solutions of the mixed reagent have been kept for more than 1 month with no precautions other than being in a glass-stoppered bottle. At the end of this period the color produced with standard nitrite solution was the same as that produced with freshly prepared reagent. Even though the reagent may become slightly colored on standing for longer than 1 month, there is little effect on its reactivity.

Standards. Solution A.—Stock Solution.—Dissolve 0.402 g. of reagent-grade sodium nitrite in 1 liter of water.

Solution B.—Dilute 5 ml. of solution A to 250 ml. with water.

Solution C.—Add 5 ml. of solution B to 80 ml. mixed reagent as noted below and dilute with this reagent to 100 ml.

Mixed Reagent. The mixed reagent consists of powders previously prepared dissolved in water. To make up 80 ml. of mixed reagent, weigh out 800 mg. of powder reagent, dissolve in water, and dilute to 80 ml. with water.

Procedure. Hold the syringe stoppered tip down and remove the plunger. Place 10 ml. of mixed reagent in the syringe. Reinsert the plunger and reset in an upright position. Expel the air in the barrel by raising the plunger, taking care not to force out the reagent and recap with the policeman. Remove the policeman and allow the plunger to fall. If the syringe is to be connected to a sampling line, which has been properly purged, hold the plunger, remove the policeman, attach the sampling line, and allow the plunger to fall. A 50-ml. air sample is drawn into the syringe. Stopper, shake, return to a safe atmosphere, and after 5 minutes compare the color produced with standards.

The shade of color produced by the nitrite obtained from fire and other air samples and that of the standards, made from sodium nitrite, are not the same. Consequently photoelectric methods cannot be employed and the concentration should be estimated by visual comparison of the color produced.

Xylenol Method.[86] In this method nitrogen oxide vapors are sampled by use of an evacuated flask containing sulfuric acid. The nitrous acid in the mixture of nitric and nitrous acids produced is oxidized to nitric acid by the use of potassium permanganate. The total nitric acid is then used to nitrate *m*-xylenol to 4-hydroxy-1,3-dimethyl-5-nitrobenzene. The latter is steam-distilled and estimated colorimetrically.

Sampling. Sample air by means of an evacuated Shepherd bottle (Fig. 5A) containing 5 ml. of sulfuric acid (5:3) and prolong the sampling period to 1 minute by use of a capillary tube side arm so that the operator can move about and obtain a more representative sample. Close the cap and set the flask aside for 2 hours to effect solution of the nitrogen oxides.

Procedure. Add a single drop, 0.05 ml., of 2 per cent potassium permanganate solution to the flask and mix thoroughly. Add 0.2 ml. of a 1 per cent solution of *m*-xylenol in propylene glycol. Allow to stand for 10 minutes. Add 100 ml. of water, some boiling chips or glass beads, and distill the nitroxylenol as detailed on page 742, trapping the distillate in a water-cooled cylinder containing 1 ml. of 2 per cent sodium hydroxide solution.

Compare the color of the distillate with solutions obtained by the distillation of appropriate quantities of potassium nitrate. One mg. of potassium nitrate is equivalent to 0.455 mg. of nitrogen oxides expressed in terms of nitrogen dioxide, NO_2.

The quantity of *m*-xylenol mentioned in the method is adequate for 0.5 mg. of nitrogen oxides. Sampling vessels of 500-ml. capacities will provide for concentrations of nitrogen dioxide up to 500 parts per million. The method is adequate for concentrations of 2 parts per million, equivalent to 5 micrograms of potassium nitrate in the standard.

d. Nitrous Oxide

It is seldom necessary to estimate the amount of nitrous oxide, N_2O, as such in air. Since, however, it is a frequently used anesthetic, it is useful to have such methods.

Determination. Absorption methods such as are used in ordinary gas analysis are not entirely suitable for nitrous oxide determinations, for there is no known substance[87] which will absorb this gas without appreciably absorbing other gases. It is appreciably soluble in the aqueous solvents used for other gases so that when it is present, it causes errors in the determination of these other gases if they are estimated by gasometric absorption methods and subsequent decreases in volume. If it is presumed to be the only contaminant present in otherwise normal air, it may be separated from the other components of air by first absorbing any carbon dioxide and water present by passing the gas through solid alkali or other solid alkaline absorbent and then condensing the nitrous oxide by passing it through a U-tube immersed in liquid air.

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[86] H. Yagoda and F. H. Goldman, *J. Ind. Hyg. Toxicol.*, *25*, 440 (1943).

[87] G. Ambler and H. R. Lunge, *Technical Gas Analysis*, Van Nostrand, New York, 1934.

Nitrous oxide is best estimated by absorbing interfering gases with dry absorbents and then reducing, oxidizing, or decomposing the nitrous oxide itself. The water vapor and carbon dioxide in air may be removed as explained, the nitrous oxide may be condensed by liquid air, or the oxygen may be removed as well as the carbon dioxide and water vapor by passing the gas through yellow phosphorus and fused potassium hydroxide.[88] The nitrous oxide may then be estimated by passing it over a heated copper gauze previously reduced by a current of hydrogen.[89] A current of hydrogen is now passed over the gauze again. The cupric oxide formed by the reaction between the nitrous oxide and the reduced copper is reduced with the formation of water. The amount of water formed is collected in a calcium chloride drying tube and is estimated gravimetrically.

Nitrous oxide may be reduced by combustion with hydrogen with a consequent contraction of 1 volume per volume of nitrous oxide.[90] Thus:

$$\underset{1\text{ vol.}}{N_2O} + \underset{1\text{ vol.}}{H_2} \longrightarrow \underset{1\text{ vol.}}{N_2} + \underset{\text{vol. negligible}}{H_2O}$$

A measured volume of pure hydrogen is added to the nitrous oxide, which has been freed from oxygen, carbon dioxide, and water. This mixture is passed over a combustion coil in a gas chamber. After completion of the combustion the coil may be removed, the water vapor formed absorbed by fused potassium hydroxide, and the volume of the remaining gases measured. The decrease in volume is a direct measure of the nitrous oxide present in the orginal sample.

Nitrous oxide may also be estimated by reduction with carbon monoxide:

$$N_2O + CO \longrightarrow CO_2 + N_2$$

While there is no volume change, the carbon dioxide may be absorbed by a dry absorbent as described and the total reduction in volume is then proportional to the volume of the nitrous oxide.

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[88] F. E. Blacet and P. A. Leighton, *Ind. Eng. Chem., Anal. Ed., 3,* 266 (1931).

[89] C. Baskerville and R. Stevenson. *Ind. Eng. Chem., 3,* 579 (1911).

[90] F. E. Blacet and D. H. Volman, *Ind Eng. Chem., Anal. Ed., 9,* 44 (1937).

It may also be estimated by thermal decomposition by passing the gas through a heated platinum capillary.[91] The gas decomposes as follows:

$$\underset{\text{2 vol.}}{2N_2O} \longrightarrow \underset{\text{3 vol.}}{2N_2 + O_2}$$

There is thus an increase in volume that is equivalent to $^1/_2$ the volume of nitrous oxide present.

2. *Ammonia*

Ammonia is an industrial hazard in numerous industries, especially where it is used as a refrigerant and may be present in dangerous concentrations if a break should occur in the refrigerating system. Among the workers who are exposed to this hazard may be mentioned coke-oven workers, textile workers, calcium carbide makers, dye makers, tannery workers, and those employed in the munitions, explosives, glue, lacquer, fertilizer, artificial ice, artificial silk, and many other industries.

Anhydrous ammonia, NH_3, is a colorless gas with a pungent odor. It boils at —33.4° C., has a specific gravity of 0.597 referred to air, and can be easily liquefied. It is extremely soluble in water, with the formation of ammonium hydroxide, a colorless liquid with a pungent odor. Strong ammonia water contains 28–29 per cent of ammonia and has a specific gravity of 0.90 at 25/25° C.

a. Physiological Response

Ammonia acts principally on the upper respiratory tract, where it exerts an alkaline, caustic action. It elicits immediate violent respiratory reflexes such as coughing and arrest of respiration. It affects the conjunctiva and cornea immediately. Inhalation causes acute inflammation of the respiratory organs, cough, edema of the lungs, chronic bronchial catarrh, secretion of saliva, and retention of urine.[92]

Concentrations of the order of 0.5–1.0 per cent by volume are lethal to men for exposures of a few minutes. Concentrations of 0.25–0.45 per cent are dangerous for exposures of 30 to 60 minutes. The maximum concentration of ammonia that can be tolerated for 60 minutes is 0.03 per cent and the maximum concentration that can be tolerated for several hours without serious disturbances is 0.01 per cent. The least detectable odor is about 53 parts of ammonia per million of air. The smallest concentration which will cause immediate irritation of the eyes is 698 parts per million and the least concentration causing coughing is 1,720 parts per million, or 0.17 per cent. [93,94] The generally accepted maximum allowable concentration is 100 parts per million of air.

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[91] H. Menzel and W. Kretzschmar, Z. *angew. Chem.*, *42*, 148 (1929).

[92] R. R. Sayers, in *International Critical Tables* (Vol. II). McGraw-Hill, New York, 1927.

b. Detection and Determination

Ammonia has adequate warning properties and, since its odor is detectable in concentrations below that causing injury, its odor can be used as a means for detection. A concentration of 0.07 mg. per liter, equivalent to 100 parts per million, will affect phenolphthalein paper immediately and litmus paper in 1 second. Concentrations of 10 parts per million will take 5 and 6.5 seconds respectively to affect these test papers.[95]

Estimation by Titration. The concentration of ammonia in air may be obtained by passing a known volume of the air through two efficient bubblers in series containing known volumes of standardized 0.02 *N* sulfuric acid. After sampling is complete, combine the solutions in the two bubblers by transfer to a titration flask and wash the bubblers well, adding the washings to the flask, or if the bubblers are of an appropriate type the titration can be made directly in the trapping device. Titrate the excess acid with 0.02 *N* sodium hydroxide solution, using methyl red indicator, 1 g. of the dye dissolved in a mixture of 50 ml. of 95 per cent alcohol plus 50 ml. of water. One ml. of 0.02 *N* sulfuric acid is equivalent to 0.00034 g. of ammonia. When other alkaline substances are present, it is best to distill the ammonia in the usual way.

A simple variation of the titration method[95a] of estimating ammonia in air is based on the computation explained in Chapter III. Air is drawn through a bubbler containing 0.01 *N* sulfuric acid with some methyl red as the indicator. This method can be used as a field test.

Procedure. Draw air at a known rate through the acid until the indicator changes at its customary pH. The amount of acid used in the bubbler is governed by the concentration of ammonia expected.

[93] A. C. Fieldner, S. H. Katz, and S. P. Kinney, *U. S. Bur. Mines, Tech. Paper 248* (1921).

[94] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem.*, *26*, 1251 (1934).

[95] E. Smolczyk, *Gasmaske, 2*, 27 (1930).

[95a] F. A. Patty, ed., *Industrial Hygiene and Toxicology* (Vol. II), Interscience, New York, 1949.

One ml. of 0.01 N sulfuric acid is equivalent to 0.00017 mg. or 0.2445 ml. of ammonia gas at 25° C. and 760 mm. Hg pressure. Hence:

$$\frac{0.2445 \times 1000 \times \text{ml. } 0.01\ N\ H_2SO_4}{\text{Rate of sampling} \times \text{min.}} = \text{Ppm. } NH_3$$

in which the rate of sampling is expressed in liters per minute and 1000 is a factor converting the milliliters of ammonia per liter of air, that is, parts per thousand, to parts per million.

When a midget impinger is used, at its standard sampling rate of 2.83 liters per minute (0.1 cubic foot per minute) and 1 ml. of 0.01 N sulfuric acid is placed in the bubbler, then the equation becomes:

$$\frac{86}{\text{Min. sampling time}} = \text{Ppm. } NH_3$$

Nessler's Method. Preparation of Folin's Nessler Reagent.[96]—Nessler's solution is an alkaline solution of the double iodide of mercury and potassium ($HgI_2.2KI$). Transfer 30 g. of potassium iodide and 22.5 grams of iodine to a 200-ml. flask; add 20 ml. of water and, after solution is complete, an excess of metallic mercury, that is, approximately 30 g. Shake the flask continuously and vigorously until the dissolved iodine has nearly all disappeared, which takes about 7 to 15 minutes. The solution becomes hot. When the red iodine solution has begun to become visibly pale, though still red, cool in running water and continue shaking until the reddish color of the iodine has been replaced by the greenish color of the double iodide. The whole operation generally takes 15 minutes. Test a portion of the solution with starch solution. Unless the starch test is positive, the solution may contain mercurous compounds. Decant the solution, washing the mercury and flask with water. Dilute the solution and washings to 200 ml. and mix well. If the cooling was begun in time, the resulting reagent is clear enough for immediate dilution with 10 per cent alkali and water and the finished solution can be used at once for nesslerization.

From this stock solution of potassium mercuric iodide prepare the final Nessler's solution as follows: To 975 ml. of an accurately prepared 10 per cent sodium hydroxide solution add the 200 ml. of the double iodide solution. Mix thoroughly and allow to clear by standing.

The 10 per cent sodium hydroxide solution should be made from a 1:1 solution of sodium hydroxide and water that has been allowed to stand until the carbonate has settled, the clear solution being decanted and used. This solution should be standardized to an accuracy of at least 5 per cent by titration and subsequent adjustment by the addition of more water or alkali as the case may be. The alkalinity of Nessler's reagent is important and should be checked against N hydrochloric acid. Twenty ml. of N hydrochloric acid should require 11 to 11.5 ml. of Nessler's solution.

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[96] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products*, Van Nostrand, New York, 1945.

Procedure. Trap the ammonia in the air in a bubbler containing 0.02 N sulfuric acid. Transfer to a volumetric flask and make to volume. Transfer from 1 to 5 ml. of this solution, according to the nitrogen content, to a 50-ml. volumetric flask, dilute to 35 ml., add 6 ml. of the Folin-Nessler reagent prepared as directed, and make to volume. Read in a colorimeter against a standard prepared by diluting 10 ml. of ammonium sulfate solution containing 0.4716 g. per liter to 100 ml. Pipette 20 ml. of this solution into a 50-ml. volumetric flask, dilute to 35 ml., add the same quantity of Folin-Nessler reagent as above, and make to volume. Each ml. of the standard solution now contains 0.004 mg. of nitrogen. If the nitrogen content of the unknown is much higher than the standard, less than 4 ml. of the unknown is nesslerized, and conversely, if the nitrogen content is much lower than the standard, more than 4 ml. is nesslerized.

This method is capable of estimating relatively low concentrations of ammonia with a high degree of accuracy.

3. Ammonium Salts

It may at times be necessary for the industrial hygienist to ascertain the amount of ammonium salts such as ammonium chloride, ammonium sulfate, ammonium nitrate, or ammonium picrate present as a fume or dust in the atmosphere. These instances arise particularly in plants where explosives are manufactured.

Ammonium Chloride. In the case of ammonium chloride it is customary to trap the compound using a midget impinger with water as the collection medium. The concentration of ammonia may then be determined on an aliquot by the Nessler method detailed above.

If desired to eliminate interferences transfer the sample solution or an aliquot to a Kjeldahl flask or a similar device, make distinctly alkaline with sodium hydroxide solution, and distill, trapping the distillate in standard acid. Titrate the excess acid with standard alkali, using sodium alizarinesulfonate as indicator. The Winkler modification may also be used by trapping the ammonia in boric acid solution, keeping the latter cool in order to avoid loss of volatile ammonium borate, and titrating the ammonia directly with standard acid, using methyl red as indicator.

Ammonium Sulfate. Ammonium sulfate may be sampled and estimated in an analogous manner.

Ammonium Nitrate. Ammonium nitrate is a common ingredient of high explosives and propellent powders. It is usually estimated in dusts by determining the ammonia content of the sample by nesslerization, as described. When the dust also contains nitrotoluene derivatives, it is necessary to make a distillation in the presence of alkali as explained above to obtain a solution clear enough for the Nessler method. Ammonium nitrate may also be estimated by the xylenol method.[97]

Procedure. Sample the air at a rate of 3 liters per minute with a midget impinger containing 10 ml. of water, sampling a minimum of 30 liters of air. Transfer a 5-ml. aliquot to a 250-ml. flask, add 0.3 ml. of 1 per cent *m*-xylenol dissolved in one of the glycol solvents, cool, and add 8.5 ml. of concentrated sulfuric acid slowly and with constant cooling to avoid a temperature of 35° C. or above. Allow the reaction to proceed for 10 minutes at room temperature, dilute with 100 ml. of water, and distill the nitroxylenol formed into a cylinder containing 1 ml. of 2 per cent sodium hydroxide solution, as described for the estimation of nitroglycerin (page 742).

Compare the yellow color of the sample with a standard made by the distillation of 500 micrograms of potassium nitrate dissolved in 5 ml. of water. One mg. of potassium nitrate is equivalent to 0.792 mg. of ammonium nitrate. The 3 mg. of *m*-xylenol added as reagent is adequate for the analysis of aliquots containing not more than 1.5 mg. of ammonium nitrate. The lower limit of sensitivity is 4 micrograms of ammonium nitrate.

Ammonium Picrate. Ammonium picrate may be sampled by use of the midget impinger with water as the collection medium. Liberate the ammonia by the addition of alkali, distill, and estimate either titrimetrically or colorimetrically with Nessler reagent. Picric acid may be determined as described on page 728.

Since ammonium picrate is a colored compound, its concentration in air may be determined by absorption in water and direct comparison with standards for there is a distinct difference in color between 10 micrograms in 10 ml. of water and 20 micrograms in the same volume of water. Collect a sample until there is a measurable color, noting the volume of air sampled, and compare with standards.

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[97] H. Yagoda and F. H. Goldman, *J. Ind. Hyg. Toxicol.*, 25, 440 (1943).

4. *Hydrazine*

It is very likely that hydrazine will find increasing use in industry and as a propellent fuel. Hydrazine, N_2H_4, is a colorless liquid, melting at 1.4° C. and boiling at 113.5° C. It is readily soluble in water and alcohol. Hydrazine forms a hydrate and also forms a series of salts with sulfuric and hydrochloric acids and with other acids. Hydrazine and its salts are poisonous. No maximum working concentrations have been established for these compounds.

The concentration of hydrazine or the hydrate in air may be estimated by trapping the compounds in water and then titrating with 0.01 *N* iodine in potassium iodide solution in the presence of sodium bicarbonate:

$$N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$$

or by titration with standard potassium permanganate solution in the presence of sulfuric acid.

$$N_2H_4 + 2O \longrightarrow N_2 + 2H_2O$$

The salts may be determined by the latter method.

5. *Nitrogen Trichloride*

Nitrogen trichloride, NCl_3, nitrogen chloride is used as a fumigant for citrus fruit and was used for the bleaching of flour but this use was prohibited after August, 1949.[97a] It is a yellowish, oily, explosive liquid boiling below 71° C. It is soluble in benzene, carbon disulfide, carbon tetrachloride, and chloroform but it is insoluble in water.

It is an irritant but is considered less irritating than chlorine. It appears to cause epileptiform seizures in dogs eating a ration containing this bleaching agent. No working standards have been evolved.

Nitrogen trichloride decomposes in hot water and it reacts with ammonia with the formation of ammonium chloride:

$$NCl_3 + 4NH_3 \longrightarrow N_2 + 3NH_4Cl$$

hence it may be estimated by a determination of the chloride ion as detailed in Chapter X.

[97a] *U. S. Food Drug Admin., S. R. A., F. D. C. 2,* rev. 1, 1949.

6. Nitrosyl Chloride

Nitrosyl chloride, NOCl, is an industrial hazard where aqua regia is used for it is evolved along with chlorine. It is also used as a flour bleach and maturation agent. It is a yellowish gas boiling at −5.5° C. and has a suffocating odor. No criteria have been established for allowable concentrations in the working room atmosphere.

It is readily decomposed by water and alkalies:

$$NOCl + 2KOH \longrightarrow KNO_2 + KCl + H_2O$$

hence it can be estimated as the nitrite by the methods detailed above or as the chloride by the methods detailed in Chapter X.

D. OXYGEN AND OZONE

1. Oxygen

Oxygen, O_2, is not a poisonous gas, but nevertheless it is in certain instances an industrial hazard, particularly if it is compressed. In this state it is an explosion hazard. Compressed oxygen is a very dangerous substance. It readily forms explosive mixtures with oils. Fieldner[98] states that an oxygen cylinder containing no more than a film of oil on its inner surface is just as truly an explosive as nitroglycerin. Instances of accidental explosions of oxygen cylinders or attached equipment are too numerous to mention. Even ordinary compressed air is subject to explosion hazard with oil, if the heat of compression is not removed by suitable coolers or if the oil has a low flash point.

Another danger is the accidental mixture of a combustible gas with compressed oxygen. Fieldner[98] cites the example of reversing the polarity of the generator in the manufacture of oxygen by the electrolytic process, with the consequent result of hydrogen going into the oxygen collecting chamber.

Determination

The industrial-hygiene chemist may be interested in the analysis of an atmosphere for the presence and amount of oxygen for two reasons. First, to ascertain whether or not an oxygen-deficient atmosphere exists and second, to ascertain whether or not oxygen is a component of a gaseous mixture or is in solution. Atmospheres containing concentrations of oxygen below 16 per cent may be detected by the use of a flame safety lamp (page 501), which is extinguished in atmospheres containing less than 16.5 per cent of oxygen.

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[98] A. S. Fieldner, *U. S. Bur. Mines, Circ. 6009* (1937).

Oxygen as a gross component of an atmosphere may be estimated volumetrically by absorption in a gas pipette by potassium pyrogallate solution, sodium hyposulfite, $Na_2S_2O_4$, solid phosphorus, or ammoniacal copper (small thin copper coils immersed in a mixture of equal volumes of saturated ammonium carbonate solution and ammonia, sp. gr. 0.96) and then noting the difference in volume produced before and after the absorption of the oxygen. For details the reader is referred to standard texts on gas analysis.

Oxygen may be estimated conveniently by absorption in a dilute alkaline mixture of sodium anthraquinone-β-sulfonate and sodium hyposulfite.[99]

Oxygen dissolved in water may be estimated colorimetrically with 2,4-diaminophenol dihydrochloride, which yields a color formed by a mixture of red, proportional to the oxygen content, and yellow, not proportional to the oxygen content.[100]

2. Ozone

Ozone is prepared on a technical scale by the exposure of air or oxygen to brush discharges. It is used industrially for bleaching oils, fats, waxes, flour, and starch; for the sterilization of drinking water; and for the purification of air.

Ozone is a powerful oxidizing agent and hence is a powerful poison. Its degree of toxicity is debatable. The generally recommended maximum permissible safe working concentration is 1 part per million of air, while DallaValle[101] quotes the figure as 0.15 part of ozone per million of air, for many persons are irritated by higher concentrations. A concentration of 0.5 part per million is objectionable because of odor. McDonnell[102] found that concentrations as low as 0.1 part per million have a powerful irritating action on the mucous membranes of the respiratory system. Scott[103] points out that there was a definitely irritating odor of ozone in the atmosphere of a photographic laboratory where an electrostatic precipitation unit was used to eliminate soot and dust, though the average ozone concentration was 0.13 part per million. Witheridge suggests[104] a maximum allowable concentration of 0.05 part per million.

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[99] L. F. Fieser, *J. Am. Chem. Soc.*, *46*, 2639 (1924).

[100] F. W. Gilcreas, *J. Am. Water Works Assoc.*, *27*, 1166 (1935).

[101] J. M. DallaValle, "Principles of Exhaust Hood Design," *U. S. Pub. Health Service*, (Aug. 1939).

[102] H. B. McDonnell, *J. Assoc. Official Agr. Chem.*, *13*, 19 (1930).

[103] R. H. Scott, *Ind. Hyg. Newsletter*, *8*, No. 9, 11 (1948).

Detection and Determination

Ozone will liberate iodine from starch-iodide paper. This test is also given by other oxidizing agents such as hydrogen peroxide, chlorine, nitrogen peroxide, etc. If, however, potassium iodide-impregnated litmus paper is used instead, the presence of ozone may be differentiated from other oxidizing agents, with the exception of hydrogen peroxide, by the formation of a blue color, as can be seen from the reaction:

$$O_3 + 2KI + H_2O \longrightarrow O_2 + 2KOH + I_2$$

The potassium hydroxide formed changes the color of the litmus paper.

Ozone is usually estimated quantitatively by passing the gas through a neutral solution or better through an alkaline solution of potassium iodide, acidifying the solution with sulfuric acid, and titrating the free iodine with 0.01 N sodium thiosulfate solution. This method is specific only in the absence of certain oxidizing agents. The greatest sensitivity that can be obtained with this method is the detection of 0.0013 mg. of ozone per ml. of 2 N potassium iodide solution.[105]

Air containing as little as 0.1 part per million by weight of ozone must commonly be analyzed. This concentration requires that 10 liters of air be passed through each ml. of potassium iodide test solution before any ozone can be detected by the above method.

Thorp[105] increases the sensitivity of the potassium iodide method by the addition of a buffer solution consisting of 5 g. of aluminum chloride, $AlCl_3.6H_2O$, and 1 g. of ammonium chloride made up to 1 liter. Five ml. of this solution is added to each 100 ml. of potassium iodide test solution before the test is made. The solution should not be acidified during the titration. The use of aluminum chloride as outlined gives a minimum sensitivity of 0.00062 mg. of ozone per ml. of potassium iodide. The potassium iodide solution so treated will have a stability of over 3 hours, which allows sufficient time for ordinary analysis. Exclusion of light from the solution will greatly increase stability, as will the use of brown bottles.

No cork or rubber should be used in contact with ozone. Not only does ozone destroy these substances, but they will seriously affect the accuracy of the determination. Ground-glass connections are preferable, but neoprene or rubber and cork coated heavily with shellac or lacquer may be used .

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[104] W. N. Witheridge, Greater New York Safety Council Convention, 1947.

[105] C. E. Thorp, *Ind. Eng. Chem., Anal. Ed.*, *12*, 209 (1940).

Only ultraviolet light will produce pure ozone. An ozonizer that uses sparks of any kind will produce pure impurities in the form of oxides of hydrogen and nitrogen. Potassium iodide will, of course, liberate free iodine in the presence of these gases. Thorp states that he has found oxide impurities as high as 75 per cent of the total yield. To make sure that only pure ozone reaches the absorption bottle containing potassium iodide solution, place a scrubbing tube containing chromic acid and a tube containing potassium permanganate in the train before the potassium iodide absorber.[106]

Procedure.[103] Draw the ozone sample through 100-ml. gas-washing bottles fitted with a glass disk disperser until a definite deep iodine color is noticed in the first bottle. Titrate with 0.01 *N* sodium thiosulfate solution standardized against resublimed iodine, using a 2–3 ml. microburette. For ozone concentrations of less than 0.5 part per million, the gas-washing bottles should be of the semimicro type and the test solution should not exceed 10 ml.

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[106] M. Bamberger and K. Trautzl, *Z. anal. Chem., 64,* 9 (1924).

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CHAPTER X

Common Poisonous Compounds of the Halogens

A. CHLORINE

1. Chlorine Gas

Chlorine gas is used in a number of industries. It is particularly hazardous where chlorine is manufactured by the electrolytic method. Chlorine is an industrial hazard among dye workers, laundry workers, employees detinning tinplate scrap, bleachers, chloride of lime makers, and in the manufacture of poison war gases such as phosgene. It is also a danger in instances where it is used as a water purifier.

Chlorine is a heavy greenish-yellow gas which has a characteristic choking and pungent odor with an irritating effect on the nose and throat. It boils at —33.6° C.; melts at —102° C.; has a density of 2.5 referred to air; and can be easily liquefied, as its critical temperature is 146° C. Its specific gravity is 1.41. Its vapor pressure at 20° C. is 6.57 atmospheres, at 30° C. it is 8.75 atmospheres, and at 40° C. it is 11.5 atmospheres. It has a high coefficient of expansion and its solubility in water at 20° C. is 215 volumes in 100 volumes.

a. Physiological Response and Toxicity

Chlorine is a strong lung irritant. It was the first chemical war gas used in World War I. A concentration of 2.5 mg. per liter breathed for 30–60 minutes will cause death. Inhalation of chlorine elicits respiratory reflexes and causes coughing, smarting of the eyes, a general feeling of discomfort in the chest, a hoarse cough, nausea, and vomiting. The face may become red and bloated because of venous congestion, or gray in color, showing failing circulation. Inhalation of chlorine affects both the lower and upper respiratory tract and produces inflammation of the entire respiratory tract and edema of the lung after severe exposure.[1] The most pronounced symptoms[2] are suffocation, constriction in the chest and tightness in the throat.

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[1] H. W. Haggard, *J. Ind. Hyg.*, *5*, 397 (1923–24).

[2] R. S. Berghoff, *Arch. Internal Med.*, *24*, 678 (1919).

Concentrations of 0.10 per cent are lethal for most animals in a few minutes. Exposure to a concentration range of 0.004–0.006 per cent for 30–60 minutes will have fatal or serious consequences. The maximum concentration to which animals can be exposed for a period of 60 minutes without serious disturbances is 0.0004 per cent and the maximum concentration to which they may be exposed for several hours without serious disturbance or with but slight symptoms is 0.0001 per cent by volume.

The least detectable odor of chlorine is 3.5 parts per million.[3] It has adequate warning properties provided one can get away from its vapors. The recommended maximum allowable concentrations are in the range of 1–2 parts per million.

b. Detection and Determination

Iodide-Thiosulfate Method. A simple method for the detection and determination of chlorine in air is to pass the air through two bubblers in series, the first containing a 4 per cent potassium iodide solution and the second containing a 2 per cent potassium iodide solution. The incoming chlorine reacts with potassium iodide, liberating iodine. Most of this is fixed by the potassium iodide with the formation of triiodide but any iodine carried out in effluent air is trapped by the second bubbler. The solutions are combined and the free iodine is titrated with 0.1286 *N* sodium thiosulfate solution. One ml. of this solution is equivalent to 1,000 parts per million of chlorine by volume at 25° C. and 760 mm. of mercury for a 1-minute sample of 1,571 ml.[4]

***o*-Tolidine Method.**[5] This is a colorimetric method which depends on the production of a yellow color by the reaction between chlorine and *o*-tolidine. It is subject to disturbing influences of small amounts of iron, manganic manganese, and nitrite nitrogen. If these interferences are present, it is better to use the iodide-thiosulfate method. If the chlorine is trapped in a series of bubblers containing water, proceed with the following method. Porter[6] recommends passing a measured volume of air through 10 ml. of *o*-tolidine reagent, prepared by dissolving 1 g. of *o*-tolidine in 100 ml. of concentrated hydrochloric acid and diluting to 1 liter. After sampling, the color produced is compared in a Nessler tube with the permanent standards as described in the method.

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[3] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem.*, *26*, 1251 (1934).

[4] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem.*, *11*, 523 (1919).

[5] *Standard Methods of Water Analysis* (8th ed.), Am. Pub. Health Assoc., New York, 1936.

[6] L. E. Porter, *Ind. Eng. Chem.*, *18*, 730 (1926).

Reagents. *o*-Tolidine Solution.—Weigh out 1 g. of *o*-tolidine (melting point, 129° C.), transfer to a 6-inch mortar and add 5 ml. hydrochloric acid (1:4). Grind the material to a thin paste and add 150–200 ml. of water. The *o*-tolidine should go into solution immediately. Transfer to a 1-liter cylinder and make up to 505 ml. Make up to the 1,000-ml. mark by adding hydrochloric acid (1:4). The reagent should be stored in amber bottles and should not be used after 6 months.

Copper Sulfate Solution.—Dissolve 1.5 g. of copper sulfate, $CuSO_4.5H_2O$, and 1 ml. of concentrated sulfuric acid in water and make up to 100 ml.

Potassium Dichromate Solution.—Dissolve 0.25 g. of potassium dichromate, $K_2Cr_2O_7$, and 1 ml. of concentrated sulfuric acid in distilled water and make up to 1 liter.

Permanent Standards. Table 13 lists the volumes of copper sulfate solution and potassium dichromate solution to be used to give standards corresponding to the chlorine contents listed. The color comparisons must be made in Nessler 100-ml. tubes having the graduation mark at 300 mm. from the bottom. If the Nessler tubes do not have the graduation mark at the 300 mm. the standards used must be checked against known concentrations of chlorine. The variation in the 300 mm. mark must not be more than ±6 mm. The standard comparison tubes should be protected from dust and evaporation by sealing on micro cover glasses with collodion, Canada balsam, or other appropriate transparent sealing material.

Determination. If the temperature of the bubbler sample solution is less than 20° C., bring a suitable volume to above that temperature but not above 40° C. by warming in a flask in hot water. Place 100 ml. of the sample, or take an aliquot and dilute to 100 ml. in a 300-mm. 100-ml. Nessler tube. Add 1 ml. of the *o*-tolidine reagent, mix and place in the dark to allow the color to develop. The sample must be placed in the dark and at no time may it be exposed to direct sunlight before the reading. The period allowed for color development should be not less than 5 minutes nor more than 15 minues, except when it is definitely shown that the maximum color development occurs and fading begins in less than 5 minutes. Compare the color developed with that of the standards under a daylight lamp or against a white background with "north" daylight. Comparisons must not be made in sunlight. Comparisons must be made by sighting from above through the liquid.

TABLE 13

Permanent Chlorine Standards

Chlorine, mg./100 ml.	Copper sulfate solution, ml.	Potassium dichromate solution, ml.
0.001	0.0	0.8
0.003	0.0	3.2
0.005	0.4	5.5
0.008	1.5	8.2
0.01	1.8	10.0
0.025	1.9	25.0
0.05	2.0	45.0
0.07	2.0	58.0
0.08	2.0	63.0
0.1	2.0	72.0

For greater quantities of chlorine, permanent standards may be made according to Table 14. The copper solution used is the same. The potassium dichromate solution contains, however, 10 times as much of the salt, that is, 2.5 g. of potassium dichromate and 1 ml. of concentrated sulfuric acid are dissolved in water and made up to 1 liter. When the standards are made according to Table 14, and 300-mm. 100-ml. Nessler tubes are used, the tubes must be filled only to a height of 240 mm. in order to give the proper comparison. These comparisons must be made by viewing from above.

TABLE 14

Permanent Chlorine Standards

Chlorine, mg./100 ml.	Copper sulfate solution, ml.	Potassium dichromate solution, ml.
0.1	8	9
0.2	8	16
0.3	8	22
0.4	8	28
0.5	8	33
0.6	8	38
0.7	8	44
0.8	8	50
0.9	8	57
1.0	8	66

Modified *o*-Tolidine Method. The official British[7] method is a modification of the *o*-tolidine method. The concentration of chlorine in an atmosphere is estimated by passing the air to be tested directly through the *o*-tolidine reagent. The hand pump apparatus and bubbler used are similar to that described for carbon disulfide (page 329).

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[7] *Dept. Sci. Ind. Research Brit., Leaflet 10* (1939).

Preparation of Reagent. Dissolve 1 g. of pure *o*-tolidine (melting point, 129–131° C.) in 100 ml. of concentrated hydrochloric acid and make up to 1 liter with water. The reagent will generally not deteriorate for 6 months.

Preparation of Standard Colors. Weigh out 1 g. of potassium dichromate, $K_2Cr_2O_7$, dissolve in water, and transfer to a 1-liter volumetric flask. Make up to volume with water. This yields a 0.1 per cent solution. Make a series of standards by diluting the following quantities of the 0.1 per cent solution to 10 ml. with water, in tubes of exactly the same bore as the bubbler:

Standard	Vol., ml., of 0.1% $K_2Cr_2O_7$ soln. diluted to 10 ml.
1	5
2	3
3	2
4	1

The standards must be well sealed or stoppered and kept in the dark. Under these conditions no change should occur in 6 months.

Procedure. Place 10 ml. of the *o*-tolidine reagent into the side arm bubbler and connect to the hand pump through a trap as previously described. The delivery tube should be approximately central and must not touch the side of the bubbler.

On entering the atmosphere to be tested, draw the strokes with the pump very slowly, using approximately 10 seconds per stroke. Continue pumping until the depth of color developed, if any, is approximately equal to that of one of the standards. Remove the bubbler and compare immediately with the standard tube, the two tubes being observed side by side by transversely transmitted daylight.

If the depth of color is the same in both tubes, the concentration of chlorine present, corresponding to the standard used for comparison and the number of strokes made, may be obtained from the following table:

No. of strokes	Standard			
	1	2	3	4
2	1/16,000	1/27,000	1/40,000	1/80,000
5	1/40,000	1/67,000	1/100,000	1/200,000
10	1/80,000	1/130,000	1/200,000	1/400,000
20	1/160,000	1/260,000	1/400,000	1/800,000
25	1/200,000	1/330,000	1/500,000	1/1,000,000

Sodium Hydroxide Modification. The *o*-tolidine method is less efficient with higher concentrations of chlorine particularly when only one bubbler is used. Wallach and McQuary[7a] found that by use of a fritted glass bubbler or a midget impinger tube containing sodium hydroxide solutions ranging from 0.0125 to 0.1 in normality, 99.9 per cent efficiency in trapping chlorine could be obtained.

Procedure. Pass air through a midget impinger tube containing 10 ml. of 0.1 *N* sodium hydroxide solution at 0.1 cu. ft. per minute. Sample 3.44 liters of air at 25° C. and 760 mm. in 1 minute and 13 seconds to give a direct reading in parts per million.

Proceed with the method detailed above for the determination of chlorine by the *o*-tolidine method but add 0.1 ml. (2 drops) of 5 *N* sulfuric acid after the addition of the *o*-tolidine to neutralize the excess alkalinity. Light transmission can be measured at 445 mμ, if desired.

2. *Hydrochloric Acid and Chlorides*

Hydrochloric acid, commercial muriatic acid, is used in many industries. The principal hazardous effects of this substance in industry are burns and dermatitis, though its importance as a respiratory irritant should not be overlooked. Hydrogen chloride, the gas from which the acid is formed, is a colorless, pungent, and poisonous substance, which is very soluble in water. It fumes very strongly in air and is extremely corrosive, for the fume is actually composed of minute droplets of hydrochloric acid. It is a gaseous by-product in a number of industries and if not properly eliminated from the effluent gas, it may be a source of air pollution. Among the industries in which it is a hazard may be mentioned the manufacture of hydrochloric acid, chlorine, and chlorine compounds and the use of the acid by etchers, engravers, metal picklers, acid dippers, and electroplaters. It is also a hazard where zinc chloride is used because of the hydrolysis of that compound with the formation of hydrochloric acid.

a. Physiological Response and Toxicity

Hydrogen chloride gas attacks the upper respiratory tract. The acid formed neutralizes the alkali of the tissues and causes death as a result of edema or spasm of the larynx and inflammation of the upper respiratory system. Concentrations of 0.13 to 0.2 per cent are lethal for human beings in exposures lasting a few minutes. Concentrations in the range of 0.1 to 0.13 per cent are dangerous if breathed for 30 to 60 minutes. The maximum concentration tolerated for exposures of 60 minutes is in the range 0.005 to 0.01 per cent and the maximum tolerated for several hours of exposure is 0.001 to 0.005 per cent.[8–10] The effect of inhalation of hydrogen chloride on animals was studied by Machle and co-workers.[10a] The maximum concentration permissible for working conditions is 10 parts per million, according to Matt.[11] The maximum allowable concentration adopted by the Conference of Governmental Hygienists in 1948 was 5 parts per million.

[7a] A. Wallach and W. A. McQuary, *Ind. Hyg. Quarterly*, 9, 64 (1948).

b. Detection and Determination

Hydrochloric acid and hydrogen chloride as well as other chlorides may be detected in air simply by trapping the fumes or dust in a standard solution of sodium hydroxide in an impinger or efficient gas-washing bottle. This absorbing solution may then be transferred to a flask and the excess sodium hydroxide determined by titration with standard sulfuric acid, in so far as the acidity is concerned. The amount of chloride may be estimated preferably by the Fajans method or by the Volhard method detailed below. Sodium carbonate solution is also used as the absorbing agent.

A refinement of the method of trapping the hydrochloric acid fumes is to draw 20 to 50 liters of air through a solution of glycerol-potassium carbonate-water in the ratio of 1:1:1 in a gas-washing bottle.[12] The chloride concentration may then be determined by the Volhard method.

Fajans Method. The use of dyes which are absorbed near the end point of a titration has been investigated by Fajans[12a] and by Kolthoff.[12b] Dichlorofluorescein is adequate for dilute chloride solutions and concentrations of the order of 0.0005 N in chloride ion may be titrated with an accuracy of 1 to 2 per cent.

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[8] K. B. Lehmann as quoted by F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

[9] Y. Henderson and H. W. Haggard, *Noxious Gases,* Reinhold, New York, 1943.

[10] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem., 26,* 1251 (1934).

[10a] W. Machle, K. V. Kitzmiller, E. W. Scott, and J. F. Freon, *J. Ind. Hyg. Toxicol., 24,* 222 (1942).

[11] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

[12] A. Heller, *Gesundh.-Ing., 55,* 261 (1932).

[12a] K. Fajans and H. Wolff, *Z. anorg. allgem. Chem., 137,* 221 (1924).

[12b] I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis. Titration Methods,* Interscience, New York, 1947.

Indicator Solution. Prepare a 0.1 per cent solution of the dye in 60–70 per cent alcohol or a 0.1 per cent solution of the sodium salt of the dye in water. About 2.5 ml. of 0.1 *N* sodium hydroxide solution is required to neutralize 100 mg. of the indicator.

Procedure. Add 2–4 drops of indicator solution to 50 ml. of the test solution. As the end point is reached the silver chloride flocculates. Near the end point the solution turns brown, when the end point is reached the color changes sharply to orange. A slight excess of silver nitrate produces a rose or red color.

Volhard Method. The thiocyanate method for the determination of chloride in which the silver chloride precipitate is removed by filtration before back-titrating may be improved by eliminating the filtration. This may be done by the use of nitrobenzene,[13] which inhibits the darkening of silver chloride in the light and improves the end point. This immiscible liquid draws the silver chloride to the interface and thus removes it from the aqueous solution, the nitrobenzene forming an insoluble layer over the precipitate.

Titrations may be made in 250-ml. glass-stoppered bottles. Twenty-five to 50 ml. of the sample solution containing from 0.048 to 0.26 g. of sodium chloride, free from the usual interfering ions, is acidified with 8 to 10 drops of nitric acid, and 1 ml. of nitrobenzene is added for each 0.05 g. of chloride. Standard silver nitrate is added until an excess of 1 to 4 ml. of 0.1 *N* solution is present. The bottle is then tightly stoppered and shaken vigorously until the silver chloride settles out in large spongy flakes. Usually 30 to 40 seconds agitation is required. A perfectly clear supernatant solution is not necessary. Fine droplets of nitrobenzene are left in suspension. However, nearly all the nitrobenzene is so closely attached to the silver chloride that there is little evidence of a separate phase.

One ml. of ferric alum indicator, prepared by adding concentrated freshly boiled nitric acid to a saturated solution of ferric alum until the solution becomes greenish yellow, is added and the titration completed with 0.05 *N* potassium thiocyanate solution. The ferric alum acts as an effective flocculating agent and coagulates any suspended matter which is present. Standard potassium thiocyanate solution is added slowly with gentle swirling until a pink color is produced. Usually a false end point appears one drop before the true end point. It fades in about 30 seconds and may be due to the desorption of the last traces of silver nitrate from the precipitate. The next drop of thiocyanate produces a decided color change which persists 10 to 15 minutes. Titration should be made at temperatures below 25°C., as is customary in other titrations with thiocyanate. If nitric acid and subsequent boiling was used in the preparation of the sample, the addition of a saturated solution of hydrazine sulfate just prior to the addition of the ferric alum indicator removes any nitrous acid formed.

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[13] J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, *7*, 38 (1935).

Diphenylcarbazide and Diphenylcarbazone Indicator for Chloride. Diphenylcarbazone was suggested as a specific indicator for the titration of chloride and bromide ions by silver ion by Chirnoaga.[14] Others[15,16] have suggested the use of both diphenylcarbazide and diphenylcarbazone with mercuric nitrate as the titrating agent. The method depends upon the formation, from mercuric ion and the indicator, of a deep blue-violet complex, after the chloride ions have combined to form slightly ionized mercuric chloride. Diphenylcarbazide is an acid-base indicator, changing from a light yellow in acid solution to a deep orange in alkaline solution, in the pH range of 6.6 to 7.4. It is probable that the alkaline form of the indicator forms the deep blue-violet complex with the mercuric ion.

Reagents. Diphenylcarbazide.—Prepare a saturated solution of diphenylcarbazide in 95 per cent alcohol. This solution gradually turns red after standing for several days and may be used as the indicator. No apparent difference results if a fresh solution of diphenylcarbazide or diphenylcarbazone solution in alcohol is used.

Mercuric Oxide.—Dissolve mercuric oxide in nitric acid (1:1) and filter. Add 8 *N* sodium hydroxide to the filtrate until precipitation is complete. Filter the precipitate and wash free from alkali. The yellow mercuric oxide may be dried over phosphorus pentoxide for 10 days, during which period it should be powdered.

Mercuric Nitrate Solutions.—Weigh out accurately the required amount of mercuric oxide necessary to make 0.1 *N* and 0.025 *N* solutions of mercuric nitrate and suspend in water. Add the calculated equivalent amount of nitric acid. To the well-stirred mixture add nitric acid dropwise until complete solution takes place. Make up to volume. The solution should be no more than 0.01 *N* with respect to nitric acid.

Determination. With 0.1 *N* mercuric nitrate solution the following procedure should be followed: The final volume of the solution in which the determination for chloride is to be made should be about 80 to 100 ml. If the chloride solution to be titrated is acid, it should first be neutralized with 0.1 *N* sodium hydroxide solution. If the acid titer is also required, 5 drops of diphenylcarbazide is added and the solution is titrated with the standard sodium hydroxide solution to an orange color. Four ml. of 0.2 *N* nitric acid is added and the solution is then titrated with 0.1 *N* mercuric nitrate solution. About 5 drops before the end point, a pink-violet color begins to develop. At the end point, 1 drop changes the color from a light violet to a deep blue-violet.

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[14] E. Chirnoaga, *Z. anal. Chem.*, *101*, 31 (1935).
[15] J. V. Dubsky and J. Trtilek, *Mikrochemie, 12*, 315 (1933).
[16] I. Roberts, *Ind. Eng. Chem., Anal. Ed., 8*, 365 (1937).

If the chloride solution is dilute and requires 0.025 *N* mercuric nitrate solution, additional precautions need be observed. The final volume should be 65 ml. ± 10 ml. If the chloride solution to be titrated is acid, 2 drops of 0.2 per cent bromophenol blue is added, and the solution is titrated with standard sodium hydroxide solution to the full blue color. Four ml. of 0.2 *N* nitric acid is added, then 5 drops of the diphenylcarbazide indicator, and the solution is titrated with 0.025 *N* mercuric nitrate solution to a definite pink color, which can be reproduced to ±0.02 ml., with the aid of a daylight lamp. The yellow color imparted by the bromophenol blue in no way interferes with the mercuric nitrate end point, and to make conditions uniform for all titrations 2 drops of bromophenol blue should be added whenever 0.025 *N* mercuric nitrate solution is used.

A blank correction should be determined with the 2 drops of bromophenol blue, 4 ml. of 0.2 *N* nitric acid, and with the nitric acid equivalent to the amount of acid in the mercuric nitrate solution used in the titration.

3. *Chlorine Dioxide*

Chlorine dioxide, ClO_2, is a dark-yellow, heavy gas, which can easily be liquefied to a red liquid boiling at 10° C. Both forms are explosive. Chlorine dioxide probably exists as such when dissolved in water but slowly hydrolyzes in water and reacts more rapidly with bases to give a mixture of equivalent amounts of chlorite and chlorate. This is analogous to the formation of nitrite and nitrate from nitrogen dioxide. Chlorine dioxide is used for water purification and for bleaching fats.

To sample chlorine dioxide use a bubbler containing 5 per cent potassium iodide solution, drawing the air through at the customary rate of 0.5 to 1 liter per minute. The amount of chlorine dioxide may then be determined iodometrically. To obtain the stoichiometrical relationships, it is best to standardize the standard thiosulfate solution against a weighed amount of the chlorine dioxide used at the plant.

4. *Chlorates*

Chlorates are used industrially in several industries such as dyeing and printing for the oxidation of colors, in the manufacture of matches, and in explosives and fireworks.

They may be sampled by use of an impinger containing water or sodium hydroxide solution. The amount of chlorate may then be estimated by a variation[17] of the ferrous sulfate-potassium dichromate or potassium permanganate method. The former has been modified to estimate small amounts of the order of milligram quantities in caustic soda solution. This can be modified for use in air analyses.

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[17] D. Williams, *Ind. Eng. Chem., Anal. Ed., 17,* 533 (1945).

Transfer a 25-ml. aliquot to a flask. Add 20 ml. of phosphoric acid (1:1) and swirl. Add 25 ml. of 0.1 *N* ferrous ammonium sulfate or ferrous sulfate in 4 *N* sulfuric acid and 25 ml. of 12 *N* sulfuric acid. Allow to stand for 10 minutes or longer, add approximately 0.5 ml. of 0.01 *M* diphenylamine sulfonic acid, and titrate the excess ferrous sulfate with 0.1 *N* potassium dichromate solution. The end point should be taken when the maximum purple color develops.

The ferrous sulfate should be standardized each time it is used and the same amount of other reagents should be used in the standardization.

To determine microgram quantities of chlorates, the following modification of the iodometric method[18] may be employed. Samples may be obtained as above but they should not be stored in rubber-stoppered bottles. No-Sol-Vit screw-cap bottles are recommended. Transfer an aliquot portion of the sample solution to the apparatus shown in Figure 90, add 1 ml. of potassium iodide solution containing 50 g. KI per liter and add sufficient water so that the total volume will be 100 ml. after the addition of the acid, as mentioned below. Add one or two glass beads to prevent bumping and connect the distillation flask to the dropping funnel. Place 50 ml. of the 5 per cent potassium iodide solution and 5 ml. of 1 per cent starch indicator solution into the receiving flask, with the receiver supported on a wooden block so as to make a liquid seal at the outlet of the condenser. Place sufficient concentrated hydrochloric acid in the dropping funnel to provide a 5-ml. excess and allow it to run into the distillation flask. Close the stopcock and light the burner. Adjust the flame so that the solution boils vigorously. Titrate the iodine as it is liberated with 0.01 *N* sodium thiosulfate solution. Continue boiling until no more iodine is liberated during a 2-minute interval.

Prepare a reagent blank by introducing 100 ml. of water, 1 ml. of 5 per cent potassium iodide solution, and one or two glass beads into the distilling flask. Acidify with 5 ml. of concentrated hydrochloric acid and distill into a mixture of 50 ml. of 5 per cent potassium iodide solution and 5 ml. of starch solution as before. The distillation should be continued until half of the water distills over. After each analysis the distillation flask should be rinsed with water, the ground-glass surfaces should be wiped, and fresh lubricant should be applied.

Iron and manganese introduce errors which should be corrected for when necessary. An empirical factor of 1.04 should be used to correct for an average recovery of 96 per cent.

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[18] D. Williams and C. C. Meeker, *Ind. Eng. Chem., Anal. Ed.*, *17*, 535 (1945).

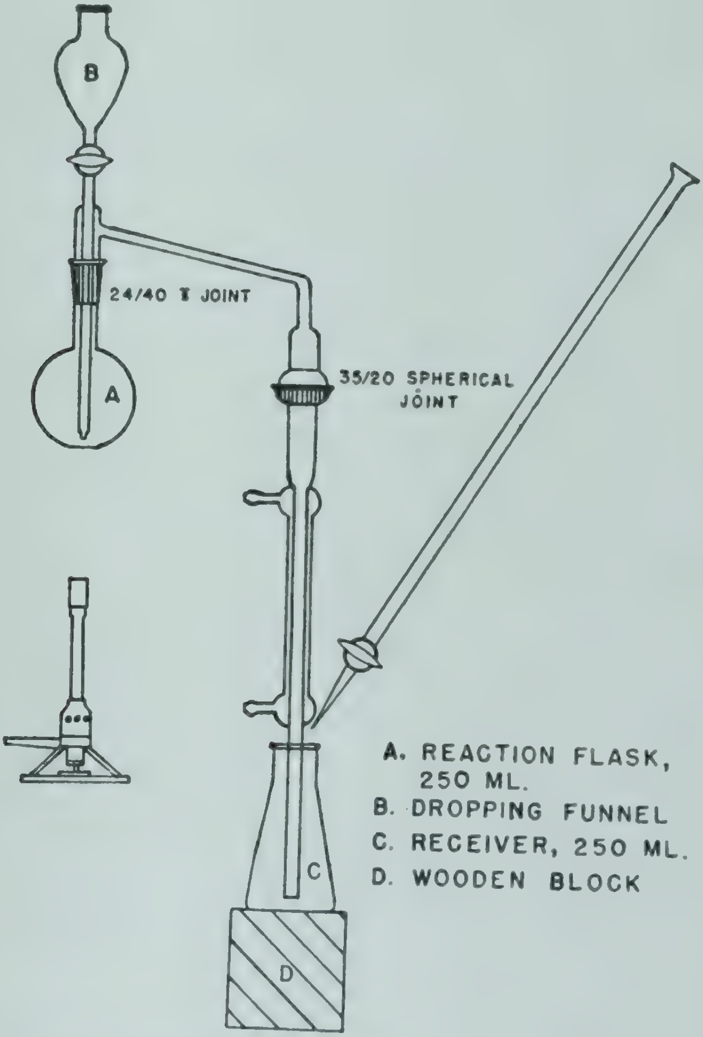
B
24/40 ₸ JOINT
A
35/20 SPHERICAL JOINT
A. REACTION FLASK, 250 ML.
B. DROPPING FUNNEL
C. RECEIVER, 250 ML.
D. WOODEN BLOCK
C
D

Fig. 90. Distillation apparatus for determination of chlorates iodometrically.

5. *Phosgene*

Phosgene, carbonyl chloride, $COCl_2$ is a colorless gas with an odor like that of musty hay. During World War I, it was used as a poison war gas and was the agent that caused more casualties than any other chemical-warfare agent. Its interest as an industrial hazard lies not only in its production as a chemical intermediate but also in the fact that phosgene is formed by the thermal decomposition of chlorinated hydrocarbons.[19] Thus it may arise in the use of carbon tetrachloride and similar types of chlorinated hydrocarbon fire extinguishers. It has been shown that carbon tetrachloride,[20-24] trichloroethylene, and other chlorinated hydrocarbons yield measurable quantities of phosgene when in contact with a flame or hot surface. The concentrations of toxic gases that arise, however, are dangerous principally in enclosed spaces like small rooms and closets and where no easy exit exists.[25]

Phosgene may be encountered in dangerous concentrations in works manufacturing organic chemical and pharmaceutical products and, in particular, dyestuffs. It is of course, an industrial hazard where it is being manufactured for industrial or war use.

At low temperatures phosgene is a liquid. It boils at 8.2° C.; freezes at −118° C.; has a specific gravity of 1.38; and a density with respect to air of 3.41, hence it is a comparatively heavy gas. It does not expand as readily as liquid chlorine. It has a low specific heat and a low heat of vaporization. It dissolves readily in many organic solvents and is, itself, a solvent for many organic chemicals. It is hydrolyzed by water with the formation of hydrochloric acid.

a. Physiological Response and Toxicity

The importance of phosgene as an industrial hazard is its toxicity. It is over ten times as toxic as chlorine, for a concentration of 0.50 mg. per liter is lethal for an exposure of 10 minutes. Serious symptoms may not develop until several hours after exposure, for the immediate symptoms produced by even a fatal dose may be relatively mild since phosgene elicits no marked respiratory reflexes; thus a person who appears to be but slightly gassed immediately following exposure may become a serious casualty several hours later. Phosgene is a lung irritant and causes severe damage to the alveoli of the lungs. This is followed by pulmonary edema, resulting in asphyxiation. Inhalation of this gas produces catching of the breath, choking, immediate coughing, tightness of the chest, slight lachrymation, difficulty and pain in breathing, and cyanosis. Its effects are probably due to hydrolysis and the formation of hydrochloric acid inside the body. It is considered in this section because of the similarity of its reactions with chlorine and hydrochloric acid The most pronounced symptoms of phosgene poisoning are coughing with bloody sputum and weakness, which may last for months.[26]

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[19] A. C. Fieldner and S. H. Katz, *U. S. Bur. Mines, Rept. Invest. 2262* (1921).

[20] E. Biesalski, *Z, angew. Chem., 37,* 314 (1924); *Chem. Abstracts, 18,* 2480 (1924).

[21] E. Stuber, *Arch. Gewerbepath. Gewerbehyg., 2,* 398 (1931).

[22] J. C. Olsen, G. E. Ferguson, V. Sabetta, and L. Scheflan, *Ind. Eng. Chem., Anal. Ed., 3,* 189 (1931).

[23] W. P. Yant, J. C. Olsen, H. H. Storch, J. B. Littlefield, and L. Scheflan, *Ind. Eng. Chem., Anal. Ed., 8,* 20 (1936).

[24] *Dept. Sci. Ind. Research Brit., Leaflet 8* (1939); *Analyst, 65,* 290 (1940).

[25] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard 2375* (1933).

An atmosphere containing 1 part by volume of the gas in 6,000 may cause lung injuries in 2 minutes, 1 part in 30,000 is very dangerous, and 1 part in 200,000 is probably fatal for exposures of 30 minutes. The maximum permissible concentration for a prolonged exposure period is about 1 part per million, that is, 0.004 mg. per liter.[27]

The least detectable odor of phosgene is 5.6 parts per million, the least concentration that affects the throat is 3.1 parts per million, the least concentration causing irritation of the eyes is 4.0 parts per million, and the least concentration causing coughing is 4.8 parts per million.[28] A concentration of 0.02–0.05 per cent is lethal to most animals in a few minutes. A concentration of 0.0025 per cent is dangerous for exposures of 30 to 60 minutes. The maximum concentration to which animals can be exposed for several hours without serious symptoms is 0.0001 per cent, or 1 part per million.[29] This is the generally accepted maximum allowable concentration.

b. Detection and Determination

Harrison's Reagent. The yellow or orange stain produced by phosgene on test paper containing diphenylamine and *p*-dimethylaminobenzaldehyde has been adopted as the standard test for the detection of phosgene in Britain.[27] The test, which is capable of detecting about 1 part of phosgene in 1,000,000 of air, is made quantitative by drawing known volumes of the atmosphere to be tested through a definite area of the test paper by means of a hand pump of specified capacity, as described on page 33, and noting the number of strokes required to produce stains of certain intensity. The concentration is then obtained by reference to standard stains on a color chart. The stains produced by phosgene are transient, and the test papers are sensitive to chlorine and hydrogen chloride. To remove traces of these gases, the atmosphere to be tested is drawn through a guard tube containing pumice impregnated with sodium thiosulfate before it comes in contact with the test paper.

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[26] R. S. Berghoff, *Arch. Internal Med.*, *24*, 678 (1919).

[27] *Dept. Sci. Ind. Research Brit.*, *Leaflet 8* (1939); *Analyst*, *65*, 290 (1940).

[28] A. C. Fieldner, S. H. Katz, and S. P. Kinney, *U. S. Bur. Mines, Tech. Paper 248* (1921).

[29] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem.*, *26*, 1251 (1934).

Patty[30] states that this phosgene test paper method is more reliable and satisfactory than any other published method for the estimation of phosgene in concentrations of 0.5 to 2 parts per million. When the paper is suspended in the atmosphere, 0.5 part per million phosgene produces a light lemon yellow color in 4–5 minutes and a dark yellow in 10–15 minutes. Higher concentrations produce proportionately greater color changes up to a dark orange shade, which occurs in about 8 minutes for 2 parts per million, and in 15 minutes with 1 part per million.

Reagent. Dissolve 5 g. of *p*-dimethylaminobenzaldehyde and 5 g. of *colorless* diphenylamine each in 50 ml. of carbon tetrachloride and mix. Dip filter papers immediately into this solution and dry. Store the papers in tightly sealed brown bottles.

Procedure. The dry paper when exposed to phosgene changes from colorless to yellow.

Nitroso Reagents. *Reagent.* Prepare two solutions and retain in separate bottles: (*A*) dissolve 0.25 g. of 1,2,4-nitrosodiethylaminophenol in 50 ml. of benzene; (*B*) dissolve 0.20 g. of *m*-diethylaminophenol in 50 ml. of benzene. The 1,2,4-nitrosodiethylaminophenol generally cannot be purchased from the usual supply houses but can be readily prepared by the following procedure: Dissolve 0.50 g. of *m*-diethylaminophenol (from the Eastman Kodak Co.) in 15 ml. of water containing 1 ml. of concentrated hydrochloric acid and cool to 0° C. Dissolve a 0.22-g. portion of sodium nitrite in 5 ml. of water and add to the phenol solution in small portions. The additions are made below the surface of the liquid, and the temperature is maintained at 0° C. at all times. This addition requires about 20 minutes. Make the mixture nearly neutral by the addition of a solution of 2 g. of sodium acetate in 5 ml. of water and then extract with 50 ml. of benzene. Filter the separated benzene layer through a dry filter paper and it is ready for immediate use as reagent (*A*).

Procedure. Mix equal parts of solutions (*A*) and (*B*) and apply to a piece of filter paper. Exposure of this paper to phosgene changes the color from brown to green. A colored "Michler's" ketone is probably formed. Its sensitivity is 0.0008 mg. per liter, or 0.2 part per million. This reaction is considered specific for phosgene. The nitroso solution is somewhat unstable and must be renewed every 3 to 4 months.

Estimation as Chloride. During World War I a method for the detection and estimation of phosgene was developed. It depends upon the absorption of the phosgene in a standard solution of alcoholic soda and the subsequent titration of excess alkali or estimation of the chloride content by some appropriate method.

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[30] F. A. Patty, *Am. J. Pub. Health,* *30,* 1191 (1940).

$$COCl_2 + 2NaOH \longrightarrow 2NaCl + CO_2 + H_2O$$

One can see that chlorides from other sources such as from chlorine or from hydrochloric acid must be absent for this method to be applicable.[31]

The gas samples to be tested may be freed from interferences by the use of zinc and mercuric sulfide rather than using silver nitrate and antimony trisulfide. The principal objection to the latter reagents is that the nitric acid formed in the removal of hydrochloric acid by the silver nitrate reacts with the antimony trisulfide to give hydrogen sulfide, which will interfere with the estimation of the phosgene. This may be obviated by passing the gas to be tested first over the antimony trisulfide and then over the silver nitrate, for any hydrogen sulfide formed by the reaction between the hydrochloric acid and the antimony trisulfide is removed, as is any free chlorine, by the silver nitrate.[32]

The gas, freed from interferences, is passed through two gas-washing bottles containing 50 ml. of alcoholic sodium hydroxide solution, prepared by dissolving 40 g. of sodium hydroxide in 125 ml. of water and adding this solution to 875 ml. of 95 per cent alcohol. After sampling is complete, neutralize with approximately N nitric acid using phenolphthalein as indicator and determine the chloride ion concentration by titration with 0.1286 N silver nitrate solution using sodium chromate solution as the indicator. One ml. of 0.1286 N silver nitrate solution is equivalent to 1,000 parts per million of phosgene (by volume at 25° C. and 760 mm. pressure) for a 1-minute sample of 1,571 ml.[33]

Standard sulfuric acid may be used to neutralize the alkali if the remaining alkali is to be estimated. This method can be improved by acidifying the absorbing solution with nitric acid and expelling the carbon dioxide by boiling before neutralizing with more alkali and titrating. It can also be improved by eliminating the use of alcohol, for aqueous sodium hydroxide absorbs phosgene effectively, is more stable, and absorbs less chlorinated hydrocarbons.[32]

Phosgene may also be absorbed in silver nitrate solution to which ammonia has been added in excess of that required to dissolve the precipitate first formed.[31] With this reagent the phosgene decomposes.

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[31] J. C. Olsen, G. E. Ferguson, V. Sabetta, and L. Scheflan, *Ind. Eng. Chem., Anal. Ed.* *3,* 189 (1931).

[32] M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed.,* *6,* 374 (1934).

[33] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem.,* *11,* 523 (1919).

forming a soluble silver ammonium chloride. On acidifying with nitric acid the silver chloride is precipitated and may be filtered off and weighed, or the excess silver may be determined by titration. Both chlorine and hydrochloric acid interfere.

Iodide-Acetone Method. Phosgene may be estimated by use of its reaction with iodide in acetone.[34]

$$COCl_2 + 2NaI \longrightarrow 2NaCl + I_2 + CO$$

Any substance capable of liberating iodine from iodide, interferes in this reaction.

Absorb the phosgene, freed from acid gases by one of the devices indicated above or as described in the following method, in a saturated solution of potassium iodide in acetone. The amount of solution to be used should contain sufficient potassium iodide so as to have a concentration several times as much as the amount of iodine that will be liberated. Add an excess of iodate and then a measured excess of 0.01 *N* sodium thiosulfate solution. Allow to stand for 1/2 hour or more. Make sure that the solution contains more water than acetone, add several drops of starch indicator, and then titrate back with 0.01 *N* iodine solution to a distinct coloration. Finally discharge the iodine-starch color with standard thiosulfate solution. The total thiosulfate solution used minus the exact equivalent of the added iodine solution, represents the amount of phosgene. Since excess iodate is present, 0.01 *N* hydrochloric acid may be used instead of the standard iodine solution.

Aniline Method. Phosgene may be estimated by a characteristic reaction with aniline, which gives quantitative results for small quantities of this gas in air.[31] Absorb the phosgene in a saturated aqueous solution of aniline. Such a solution contains about 26 g. of aniline per liter of water. In this reaction diphenylurea is formed when excess aniline is present, according to the following equation:

$$4C_6H_5NH_2 + COCl_2 \longrightarrow CO(NHC_6H_5)_2 + 2C_6H_5NH_2.HCl$$

The diphenylurea is only slightly soluble in water as well as in a saturated aqueous solution of aniline, and may be filtered off, washed with cold water, dried at 70–80° C., and weighed. Hydrochloric acid interferes by conversion of the aniline into aniline hydrochloric and chlorine by oxidizing the aniline to insoluble compounds.

Pass air through a purifying tube, a 5-cm. glass U-tube with arms 22 and 30 cm. long. The short arm of the purifying tube contains 6 cm. of absorbent cotton at the top where the gas enters and below the cotton 12 cm. of 10- to 12-mesh calcium chloride, previously neutralized with hydrogen chloride gas. A small amount of cotton is placed in the connection between the two arms of the U-tube. The long section of the purifying tube contains 10 cm. of amalgamated mossy tin at the bottom, then 3 cm. of mossy tin, and at the top, 15 cm. of closely packed mossy zinc. Each sample is then led through two simple absorption tubes of the petticoat (hoopskirt or inverted thistle tube) bubbler type in series, each of which contains 25 ml. of the phosgene absorbent. The purifying train and connections to the absorption bottles should be purged with the test atmosphere before sampling.

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[34] M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed., 6,* 457 (1934).

In preparing the absorption solution an excess of aniline is kept in a bottle of water for 1 week with occasional shaking, then phosgene is passed through the solution until a permanent precipitate of diphenylurea is formed and the mixture is kept ready for use. Dipenylurea can be bought commercially and the saturated solution may be prepared without the aniline-phosgene reaction.

When a determination is to be made some of the solution is filtered several times through a Gooch crucible and 25-ml. portions are placed in each of the bubblers. After the measured volume of sample is passed through the bubblers they are allowed to stand 2 hours and the aniline reagent is then filtered through a tared prepared Gooch crucible. Any precipitate which adheres to the sides of the absorption flasks is dissolved in warm alcohol and evaporated almost to dryness in a small beaker on a steam bath. Several ml. of water is added and the evaporation is continued until there is no longer an odor of alcohol. This additional precipitate is then washed, with thorough policing, into the prepared Gooch crucible and the entire precipitate is washed thoroughly with a solution of 1 *N* hydrochloric acid saturated with pure diphenylurea. The precipitate is then aerated several minutes and finally dried at 70–80° C. to constant weight.

The diphenylurea is extracted from the Gooch crucible by washing with several portions of boiling ethyl alcohol and the crucible is again dried at the same temperature to constant weight. The alcoholic extract is then dried in a tared weighing bottle, first to dryness at room temperature and then to constant weight at 70–80° C. These final weights may be used in calculating the phosgene content of the air sampled.

At a room temperature of 23° C. and a barometric pressure of 740 mm. of mercury, 1 mg. of diphenylurea is equivalent to 0.1175 ml. of phosgene. This value may be calculated in parts of phosgene per million parts of air by volume as follows:[35]

$$1 \text{ mg. of diphenylurea} = \frac{0.1175 \times 1{,}000}{\text{liters of sample}} \text{ ppm.}$$

B. BROMINE

The use of bromine and bromides in industry is increasing with the development of cheaper methods of production. Among the workers exposed to the hazard of these chemicals may be mentioned photographic-film makers, tetraethyl lead gasoline workers, and those employed in the manufacture of war gases of the tear-gas type like bromobenzylcyanide and bromoacetone. Other industries are those engaged in the manufacture of brominated dyes and colors, brominated drugs, and other organic chemicals. Bromine is used in the manufacture of refrigerants, fumigants, and germicides; it is used in the extraction of gold and as a depolarizer in batteries.

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[35] W. P. Yant, J. C. Olsen, H. H. Storch, J. B. Littlefield, and L. Scheflan, *Ind. Eng. Chem., Anal. Ed., 8,* 20 (1936).

The organic derivatives of bromine, methyl bromide, ethyl bromide, etc., will be discussed in the chapter on halogenated hydrocarbons, Chapter XV.

Bromine is a dark red, almost black, heavy liquid. Its vapor is also dark red in color. It boils at 58.7° C. but vaporizes readily at room temperature. It has a specific gravity of 3.12 at 15/15° C. and its density with respect to air is 5.5. It is soluble in water, 1 ml. of bromine dissolving in about 30 ml. of water. It is readily soluble in alcohol, ether, chloroform, benzene, and many other organic solvents.

a. Physiological Response

The fumes of bromine are highly irritating to the eyes and the respiratory tract, both upper and lower sections. It has an oxidizing action and elicits respiratory reflexes. Inhalation causes inflammation of the entire respiratory system with edema of the lungs after severe exposure.[36]

The least detectable odor of bromine is of the order of 3.5 parts per million; the least concentration causing irritation of the throat is 15.1 parts per million and 30.2 parts per million will cause coughing.[37] A concentration of 1,000 parts per million will be lethal for men for exposures of a few minutes. Concentrations in the range of 40 to 60 parts per million are dangerous to life after exposures of from 30 to 60 minutes. The maximum concentration that can be tolerated for an exposure of 60 minutes is 4 parts per million and the maximum that can be tolerated for several hours without serious symptoms is 1.0 part per million. The latter concentration is the generally accepted maximum allowable concentration.

b. Detection and Determination

A simple method for the detection and estimation of bromine and inorganic bromides in air is to pass the air through a gas washing bottle containing a cold solution of potassium hydroxide:

$$Br_2 + 2KOH \longrightarrow KBr + KBrO + H_2O$$

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[36] H. W. Haggard, *J. Ind. Hyg., 5,* 397 (1923–24).

[37] A. C. Fieldner, S. H. Katz, and S. P. Kinney, *U. S. Bur. Mines, Tech. Paper 248* (1921).

Add some hydrogen peroxide to react with the hypobromite,

$$KBrO + H_2O_2 \longrightarrow KBr + H_2O + O_2$$

and then estimate the bromide as silver bromide. The Kolthoff and Yutzy method,[38] in which the bromide is oxidized to bromate and subsequently estimated iodometrically, is described on page 603.

Bromine vapor can be caught completely[39] using a single sintered-glass bubbler containing 3 per cent potassium iodide solution when sampled at a rate of $^1/_2$ liter per minute. The liberated iodine can be determined by titration with 0.01 N thiosulfate using starch as indicator.

C. FLUORINE

1. *Hydrofluoric Acid*

The use of this acid directly and its occurrence as a by-product in industry is increasing and consequently the dangers associated with its use are more prevalent. This acid is used in the etching of glass and in the production of clouded glass, as in opalescent electric light bulbs. The use of hydrofluoric acid for clouding of glass is diminishing and is being replaced by sand blasting. Other industries using this acid are silicate extraction, phosphorus extraction, and gold refining. It is a particular hazard in the electrolytic production of aluminum. In this instance hydrogen fluoride occurs as a by-product during the electrolysis of bauxite, a hydrated alumina, $Al_2O_3.2H_2O$, in molten cryolite, Na_3AlF_6, a double fluoride of aluminium and sodium, also written in symbols as $3NaF.AlF_3$.

Hydrogen fluoride is a colorless liquid boiling at 19.4° C. It is very soluble in water and fumes very strongly in moist air, being similar to hydrogen chloride in this respect. The water solution yields hydrofluoric acid. At low temperatures the vapor of hydrogen fluoride is dimeric and corresponds to the formula H_2F_2.

a. Physiological Response

Hydrofluoric acid is violently corrosive. It attacks the skin vigorously, yielding slowly healing sores. Inhalation of the vapor causes a sense of constricted breathing, coughing, and irritation of the throat. The vapor causes ulceration of the mucous membranes and may cause chemical pneumonia. It may attack the eyes, causing conjunctivitis.

The effect of hydrogen fluoride on guinea pigs and rabbits was studied by Machle[40] and his co-workers. The recommended maximum allowable concentration for this compound ranges from 1.5 to 3.0 parts per million.

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[38] I. M. Kolthoff and H. C. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, *9*, 75 (1937).

[39] F. H. Goldman and J. M. DallaValle, *U. S. Pub. Health Repts.*, *54*, 1728 (1939).

[40] W. Machle, F. Thamann, K. Kitzmiller, and J. Cholak, *J. Ind. Hyg.*, *16*, 129 (1934).

b. Detection and Determination

Hydrofluoric acid vapor may be caught in gas-washing bottles, preferably coated with paraffin, containing sodium hydroxide solution, or it may be sampled as detailed under the section on fluorides. Various tests have been devised for the detection of hydrogen fluoride. Some of these are discussed on page 394.

Direct Titration. Machle[40] and his co-workers estimated the amount of hydrogen fluoride in air by direct titration with standard nitric acid solution.

They used a special two-bulb three-stopcock sampling apparatus (Fig. 91). The small bulb contained sufficient standard sodium hydroxide solution to absorb 5 times the amount of hydrogen fluoride expected. The large bulb is evacuated to 1 mm. The sample is taken so that it is drawn through the small bulb and the sodium hydroxide reagent and is sprayed against the sides of the large bulb by the force of the incoming mixture, thus protecting the glass against etching. The volume of the sample is obtained by calculation from the pressure after evacuation, the pressure after sampling, and the barometric pressure, as previously explained.

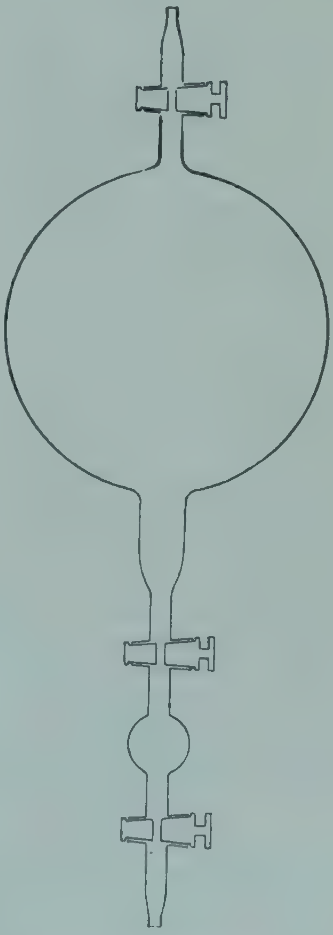
Fig. 91. Sampling apparatus for hydrogen fluoride.

The bulb is shaken well to complete absorption and about 80 per cent of the sodium hydroxide solution is titrated with standard nitric acid solution using 2 ml. of 0.04 per cent phenol red solution as indicator, the solutions being titrated at the boiling point to a clear-yellow end point.

A like amount of sodium hydroxide solution used to fill the small bulb is titrated in an identical manner. The difference between the two titrations, after correcting for the aliquot of test solution used, represents a decreased total alkalinity attributable to the absorption of hydrogen fluoride. The results, corrected to 760 mm. of mercury and 25° C., are expressed in terms of mg. per liter as follows:

$$\frac{\text{mg. } H_2F_2 \text{ equivalent to decrease in fixed alkali}}{\text{liters of sample corrected to } 25^\circ \text{ C. and 760 mm.}} = \text{mg. } H_2F_2\text{/liter at } 25^\circ \text{ C. and 760 mm.}$$

For conversion to parts per million, multiply mg. by 1.223.

2. *Fluorides*

The two principal fluorides used in industry are cryolite, a sodium aluminum fluoride, $3NaF.AlF_3$, and fluorspar or fluorite, a calcium fluoride, CaF_2. Cryolite is used widely as an agricultural insecticide.

Fluorides are used in aluminum and magnesium foundries, in the welding of aluminum and of alloy steels, in glass manufacture, and in alkylation plants, as well as in other industries. Fluorides may occur in industrial processes as dusts, fumes, and vapors. Dusts are adequately sampled by the use of the midget impinger, fumes by use of the electrostatic precipitator, and vapors by employing a fritted bubbler.

The maximum allowable concentration is considered to be 2.5 mg. per cubic meter of air. Harrold,[41] however, considers this value too high, for such concentrations are said to have caused dermatitis. He recommends a value of 1.0 mg. per cubic meter (10 mg. per 10 cubic meters) as the proper maximum allowable concentration.

a. Detection

Various test papers have been suggested for the detection of fluorides in air. One of these, devised by Harrold,[42] employs a pump. The test paper is immersed in an activating solution, is inserted in the holder of the pump, and the number of strokes necessary to produce a detectable color change is noted. The fluoride concentration may be read from a chart.

A qualitative test[42a] has been devised which depends on the insolubility of thorium fluoride and the intense red color of the lake of alizarinsulfonate adsorbed on thorium hydroxide. If fluorine is absent the lake forms and a red color is observed. If fluorine is present thorium fluoride is formed and no color is detected. The test has been adapted for the detection of fluorine in organic fluorides.

b. Determination

Distillation Method. The determination of fluorine as developed by

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[41] G. C. Harrold, *personal communication*, 1948.

[42] Production Equipment Co., Detroit 2, Mich.

[42a] E. L. Bennett, C. W. Gould, Jr., and E. H. Swift, *Anal. Chem.*, *19*, 1035 (1947).

Willard and Winter[43] is based on the isolation of fluorine accurately and expeditiously from interfering materials by distillation as hydrofluosilicic acid, which may be subsequently estimated colorimetrically by the bleaching of a zirconium-alizarin lake or by titration with thorium or cerous nitrate. If ashing has to be performed in order to free trapped fluorine dust of organic material, the fluorine will be lost in the ashing or will not be completely volatilized when the ash in distilled with sulfuric acid. A five per cent magnesium acetate solution[44] should be used to moisten the material to be ashed. Dry the material in an oven for at least 24 hours and ash in a muffle at dull redness. Brush the ash into the distillation flask.

Apparatus. The distillation apparatus (Fig. 92) consists of a Claissen flask with necks 10 cm. long instead of the usual length, connected with an upright condenser. The side arm that connects the flask with the condenser is bent upward for about 4 cm. and then downward at two points in order to fit the vertical condenser. Preferably the side arm should fit the condenser by a ground-glass joint. More elaborate trapping devices are inadvisable because the possible adsorption on the glass of fluorine causes fluorine deficiencies. The straight neck of the distilling

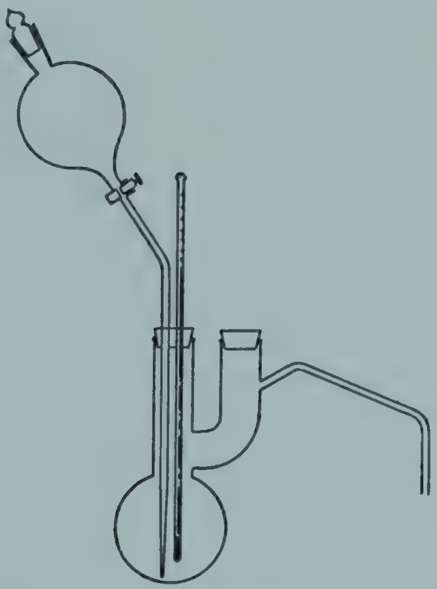

Fig. 92. Fluorine distillation apparatus.

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[43] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed., 5,* 7 (1936).
[44] O. B. Winter, *J. Assoc. Official Agr. Chem., 19,* 362 (1936).

flask carries a rubber stopper fitted with a thermometer and a dropping funnel whose stem has been drawn to a capillary. Both the thermometer and the dropping funnel extend to within 5 mm. of the flask bottom.

Distillation Procedure. Evaporate the trapping solution to 50 ml., if the volume is greater than that, and transfer to the distilling apparatus, or wash the ashing crucible or dish several times with water and a small amount of sulfuric acid, after having brushed the ash into the distillation flask. Connect the apparatus as directed above. Remove the stopper and add concentrated sulfuric acid until the effervescence ceases or until the mixture is distinctly acid and then add approximately 12 ml. more of sulfuric acid. Sufficient water should be added so that the mixture will begin to boil at 110° C. Replace the stopper, boil, and distill, allowing the temperature to rise to 135–140° C., collecting the distillate in a 100-ml. volumetric flask. When the temperature of the liquid being distilled reaches 135° C., sufficient water is slowly dropped from the funnel to compensate for the water distilling out and in this manner the temperature is maintained at 135° C. The distillation requires constant supervision. After the 100-ml. flask is filled (distillate 1), collect another 50 ml. (distillate 2) to be certain that all the fluorine has been volatilized.

It has been shown that phosphates interfere in the determination of fluorine by distillation as hydrofluosilicic acid,[45] for it is at times possible that the phosphates are reduced to a form which is readily carried over in the distillate. In such an instance, a double Willard-Winter distillation of the fluorine from the ash should be made. The first distillation should be made with sulfuric acid to eliminate hazard, especially when carbonaceous matter is present, and the second may be made with perchloric acid at 135° C. This procedure yields a distillate free from sulfate and phosphate. Great care should be exercised in all distillations and operations using perchloric acid because of danger from explosion.

Colorimetric Method. Dissolve 0.87 g. of zirconium nitrate, $Zr(NO_3)_4 \cdot 5H_2O$, in 100 ml. of water and 0.17 g. of sodium alizarinate in 100 ml. of water. Mix equal parts of the two solutions and dilute the mixture (1:4) with water.

Make up a series of standards in Nessler tubes or test tubes of about 80-ml. capacity by placing 0.02, 0.04, 0.06, 0.09, 1.20 mg. of fluorine in each tube, respectively, prepared from lithium fluoride 0.02 *N* solution, containing 0.5188 g. per liter of lithium fluoride, or from specially purified sodium fluoride (made from sodium carbonate and hydrofluoric acid) 0.02 *N* solution, containing 0.840 g. per liter. Add water to make about 50 ml. and 10 ml. of hydrochloric acid (1:1), mix thoroughly, add 2 ml. of the dye solution, and bring all the tubes to the same level with water. Again mix thoroughly, place the tubes in a steam bath for 30 minutes, and cool. For unknowns take aliquots of the distillates whose fluorine contents fall within the above range of standards. The fluorine is determined from the nearest standard.[46]

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[45] H. V. Churchill, R. W. Bridges, and R. J. Rowley, *Ind. Eng. Chem., Anal. Ed.*, 9, 222 (1937).

The fading of the zirconium-alizarine lake is a measure of the amount of fluorine present.[47] If quantities of fluorine fall below the range given less dye should be used, and if quantities above the range are to be determined more dye should be used.

The individual tubes show a fading in color, which increases as the fluorine content increases, hence a comparison of the fading caused by an aliquot of the unknown with the standards prepared gives the measure of the fluorine content of the sample.

Titrimetric Method. *Cerous Nitrate Modification.*[48] Several drops of 0.04 per cent phenol red solution are added to the distillate obtained as detailed in the foregoing and the liquid is neutralized with dilute sodium hydroxide solution, avoiding a large excess. The alkaline solution is boiled and repeatedly brought back to the apparent neutral point with 0.02 *N* or 0.01 *N* perchloric acid. During this neutralization, the volume is reduced to 5 to 10 ml. When the faint pink color is no longer restored by boiling (carbonate free), the solution is cooled, transferred quantitatively to a 50-ml. beaker, and concentrated from about 25 ml. down to 2 to 3 ml. with the aid of a hot plate. Two drops of a saturated alcoholic solution of methyl red and 10 drops of 0.04 per cent bromocresol green solution are added. The bromocresol green is weighed out exactly and neutralized with standard sodium hydroxide to yield the monosodium salt. This prevents the alteration of the neutrality of the solution when the indicator is added. The liquid is titrated at 80° C. to the maximum red color with cerous nitrate solution, 1 ml. of which is equivalent to 0.5 mg. of fluorine. When the amount of fluorine is less than 0.2 mg., 0.01–0.02 *N* thorium nitrate solution may be substituted for the cerous nitrate.

Thorium Nitrate Modification.[49] The thorium nitrate solution may be standardized by titration against known volumes of 0.02 N fluoride solution. Transfer a known aliquot of standard 0.02 N fluoride solution to a flask, add water to bring the volume to 20 ml., and then add an equal volume of ethyl alcohol. Add 6 drops of alizarin red indicator (prepared by dissolving 1 g. of sodium alizarinsulfonate in 100 ml. of ethyl alcohol, filtering off the residue, and making up the filtrate to 250 ml. with alcohol) and then only enough dilute hydrochloric acid to destroy the color. Avoid excess acid. Titrate with the thorium nitrate solution over a white surface in a good light to a faint permanent reappearance of color. Titrate slowly near the end point. Run a blank titration on the indicator by determining the volume of standard 0.02 N fluoride solution necessary to cause disappearance of color in a slightly acid water-alcohol solution of 6 drops of the indicator and compare this with the volume of standard thorium nitrate necessary to discharge the color. Calculate the strength of the thorium nitrate solution by use of the following equation:

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[46] N. Allen and N. H. Furman, *J. Am. Chem. Soc., 54,* 4625 (1932).
[47] O. M. Smith and H. A. Dutcher, *Ind. Eng. Chem., Anal. Ed., 6,* 61 (1934).
[48] E. W. Scott and A. L. Henne, *Ind. Eng. Chem., Anal. Ed., 7,* 299 (1935).
[49] C. S. Boruff and G. B. Abbott, *Ind. Eng. Chem., Anal. Ed., 5,* 236 (1933).

$$1.0 \text{ ml. } Th(NO_3)_4 = \frac{\text{ml. of } 0.02\ N\ F^- \text{ soln.}}{\text{ml. of } Th(NO_3)_4 \text{ soln.}} \times 0.38 = A \text{ mg. of } F^-$$

The unknown distillates may be titrated in a similar manner by making alkaline, neutralizing, and concentrating as described above. Add 6 drops of indicator, dilute acid until the color of the indicator just disappears, and then an equal volume of alcohol. The solution should be only faintly acid. If no fluorides are present the color will not be discharged. Titrate at once, if fluorides are present, with the standardized thorium nitrate solution to the faint reappearance of the pink color.

Williams Modification. The thorium nitrate titration of fluorides has been simplified by Williams[50] by using a single titration against a permanent color standard. It is suitable for microgram quantities. Higher concentrations may be estimated by the Matuszak and Brown variation.[51]

Reagents. Acidified Standard Thorium Nitrate Solution.—Stock Solution.—Dissolve 1.27 g. of thorium nitrate, $Th(NO_3)_4.4H_2O$, and 72 ml. of N hydrochloric acid in water and make up to 100 ml.

Dilute Solution.—Dilute 5 ml. of the stock solution to 500 ml. with fluorine-free water. One ml. of the dilute solution is equivalent to 5 micrograms of fluoride.

Acid-Indicator Solution.—Dissolve 0.020 g. of sodium alizarinmonosulfonate (alizarin-S) in water, add 100 ml. of the dilute acidified thorium nitrate solution and 14.3 ml. of *N* hydrochloric acid, and make up to 200 ml. Two ml. of this solution added to 50 ml. of fluorine-free water and 10 ml. of 2 *N* sodium chloride solution in a Nessler tube should give the correct end-point color; if not, impurities in the salt or other chemicals may be responsible and the proportion of the dilute standard thorium nitrate solution used should be modified accordingly. The color should be judged when making the acid-indicator solution, for it is likely to alter on standing.

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[50] H. A. Williams, *Analyst, 71,* 175 (1947).

[51] M. P. Matuszak and D. R. Brown, *Ind. Eng. Chem., Anal. Ed., 17,* 100 (1945).

2,5-Dinitrophenol Indicator Solution.—Prepare a 0.05 per cent aqueous solution.

Color Standards. Temporary.—Dilute an aliquot of a standard fluoride solution (made from sodium fluoride prepared from the purest sodium carbonate and hydrofluoric acid) containing 100 micrograms of fluorine to 50 ml. with water. Add 10 ml. of 2 *N* sodium chloride solution, 2 ml. of the acid-indicator solution, 20 ml. of the dilute standard thorium nitrate solution, and mix. This color is stable for several hours.

Permanent.—Mix 3 ml. of 10 per cent hydrochloric acid with 50 ml. of a solution containing 1 per cent of cobalt chloride, $CoCl_2$, add 30 ml. of 0.1 per cent potassium chromate solution, and dilute to 100 ml. Dilute 3 ml. of this stock mixture with water to a volume approximately equal to the anticipated volume of the test solution when titrated. The color should be identical with that of the temporary standard. If it is not, possibly because of differences in the thorium nitrate used, the proportions of the components should be adjusted until a match is obtained. Alternatively, alizarin-S may be used as a color standard in a buffered solution of suitable pH.

Procedure. Add 3 drops of 2,5-dinitrophenol indicator solution to an appropriate aliquot of the distillate or fluoride solution in a Nessler tube and add 0.05 *N* sodium hydroxide solution until the solution when mixed assumes a faint yellow color. Then add 1 drop or sufficient 0.01 *N* hydrochloric acid solution to just discharge the color. It is useful to have a Nessler tube containing water for comparison, for the color becomes very pale near the end point. If the presence of free halogen is suspected, add 1 ml. of 1 per cent hydroxylamine hydrochloride solution just before the neutralization.

Transfer accurately 50 ml. of the neutralized solution, containing between 0.5 and about 150 micrograms of fluorine, to another Nessler tube, add 10 ml. of 2 *N* sodium chloride solution and 2 ml. of the acid-indicator solution, and mix. Titrate with the dilute standard thorium nitrate solution until the color exactly matches that of the standard color solutions. For a 5-g. sample, 1 ml. of dilute thorium nitrate solution is equivalent to 1 part per million, subject to correction blanks.

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CHAPTER XI

Carbon Monoxide, Carbon Dioxide, Cyanides, and Nitriles

The gases containing carbon are the most numerous of industrial hazards. We have already had occasion to discuss phosgene, or carbonyl chloride, carbon disulfide, nickel carbonyl, iron carbonyl, etc., because of their relationship to other gases and elements. In this chapter, other carbon compounds, namely carbon monoxide, carbon dioxide, cyanogen, and hydrogen cyanide, will be discussed.

A. CARBON MONOXIDE

The carbon compound which is the most important industrial hazard is carbon monoxide. Indeed, it has been said that carbon monoxide is now, and has been since the first discovery of fire, the most widespread poison connected with human life and activity.[1-3] Only the means by which a person is poisoned by this substance has changed.

1. Industrial and Nonindustrial Hazard

This gas is met in any industry in which there is the possibility of incomplete combustion of carbon compounds or carbonaceous material. Not only is carbon monoxide an important industrial poison but it is also the greatest single nonindustrial hazard because it is a component of nearly all types of illuminating and heating gas, it is a component of the exhaust gases of automobiles, and it is a probable component of the flue gas produced by whatever form of heat is used in the home—wood, coal, illuminating gas, or oil.

For these reasons carbon monoxide is a hazard in the home, in the private garage, and in the street, as well as in the public garage and in the shop.

Dublin and Vane[4] list over one hundred industries in which carbon

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[1] L. Lewin, *Die Kohlenoxydvergiftung,* Berlin, 1920.
[2] H. S. Forbes, *J. Ind. Hyg., 3,* 11 (1921).
[3] R. C. Frederick, *Analyst, 56,* 561 (1931).
[4] L. I. Dublin and R. J. Vane, *U. S. Dept. Labor, Div. Labor Standards, Bull. 41* (1941).

monoxide poisoning is a hazard. A comprehensive review of the hazards and mechanism of action of carbon monoxide is given by von Oettingen.[4a] Table 15 lists the approximate amount of carbon monoxide in gases which may be present at several common sources of poisoning by this substance.

TABLE 15

Carbon Monoxide Content[5,6]

Type and Source	CO by volume, per cent
Mine explosion, immediately after dust explosion (exptl.)	8.0
Mine explossion, 1 day after explosion in coal mine	1.0
Mine fire	1.0
Blasting with 40% gelatin dynamite, 7 min. after shooting 100 sticks	1.2
Blasting, products of combustion	
Black blasting powder	10.8
40% nitroglycerin dynamite	28.0
40% ammonia dynamite	5.0
TNT	60.0
Blast-furnace stack gas	28.0
Bessemer-furnace gas	25.0
Crucible furnace; gas fuel melting Al-Cu-Sn alloy	5.5
Arc furnace melting aluminum	32.2
Cupola gas	17.0
Coke-oven gas	6.0
Coal gas	16.0
Carbureted water gas	30.0
Blau gas (cracked heavy oils)	40.0
Producer gas from coke	25.0
Distillation coal oil mixtures	7.4
Producer gas from oil	5.0
Fuel gas	30.0
Gas range burning natural gas	0.2
Room heater burning natural gas	0.5
Automobile exhaust gas (average of tests of 101 cars of all types)	7.0
City fire (black smoke from burning buildings)	0.1
Insulation burning in electric arc	0.5
Furnace gas of small-house heating and hot-water system	1.0
Railroad-locomotive stack gas	2.0

Carbon monoxide is a colorless and odorless gas. It is combustible and is lighter than air, having a specific gravity of 0.967. It used to be termed "white damp" by miners but that is an inappropriate term. Air containing 12.5 to 74 per cent of carbon monoxide will explode if ignited.[7,8] Therefore 12.5 per cent and 74 per cent are known as the upper and lower explosive limits.

[4a] W. F. von Oettingen. *U. S. Pub. Health Service, Bull. 290* (1944).

[5] R. R. Sayers and S. J. Davenport. *U. S. Pub. Health Service, Bull. 195* (1937)

[6] R. R. Sayers and W. P. Yant. *U. S. Bur. Mines, Rept. Invest. 2476* (1923).

2. *Physiological Response and Toxicity*

Carbon monoxide in excess of 0.01 per cent will produce symptoms of poisoning if breathed for a sufficiently long time. As little as 0.02 per cent will produce slight symptoms in several hours. Four parts in 10,000, which is equivalent to 0.04 per cent, will produce headache and discomfort within 2 to 3 hours. With moderate exercise 0.12 per cent will produce slight palpitation of the heart in 30 minutes, a tendency to stagger in $1^1/_2$ hours, and confusion of mind, headache, and nausea in 2 hours. A concentration of 0.20 to 0.25 per cent will usually produce unconsciousness in about 30 minutes. Its effects in high concentrations may be so sudden that a man has little or no warning before he collapses.[9] These symptoms are summarized in Table 16.

TABLE 16

Carbon Monoxide Poisoning[10,11]

Effect	CO, per cent
Allowable for an exposure of several hours	0.01
Can be inhaled for 1 hour without appreciable effect	0.04–0.05
Causing a just appreciable effect after 1 hour's exposure	0.06–0.07
Causing unpleasant but not dangerous symptoms after 1 hour's exposure	0.1–0.12
Dangerous for exposure of 1 hour	0.15–0.20
Fatal in exposure of less than 1 hour	0.4 and above

Carbon monoxide is really an asphyxiant and not a poison because it produces its harmful effect by combining with the hemoglobin of the red cells to form a relatively stable compound, carbon monoxide hemoglobin, usually abbreviated HbCO, thus preventing this combined hemoglobin from taking up oxygen to form oxyhemoglobin, abbreviated HbO_2, and thus depriving the body of its oxygen. The affinity of carbon monoxide for hemoglobin is about 300 times that of oxygen. Hence, if only a small amount of carbon monoxide is present in the air taken into the lungs,

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[7] H. F. Coward and G. W. Jones, *U. S. Bur. Mines, Bull. 279* (1928).

[8] G. W. Jones, *U. S. Bur. Mines, Tech. Paper 450* (1929).

[9] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines, Miners' Circ. 33* (1938).

[10] R. C. Frederick, *Analyst, 56*, 561 (1931).

[11] Y. Henderson and H. W. Haggard, *Noxious Gases*, Reinhold, New York, 1927.

the carbon monoxide will be absorbed in preference to the oxygen by the blood. Since carbon monoxide is not definitely a poison, it does not have much effect on the body. However, carbon monoxide asphyxia, and probably other types of asphyxia, produces degenerative changes in nerve cells and throughout the entire brain.[12]

The percentage of hemoglobin of the blood combined with carbon monoxide instead of with oxygen is termed "percentage of blood saturation". Symptoms of poisoning more or less parallel the blood saturation. The first decided symptoms during rest make their appearance when 20 to 30 per cent of the hemoglobin is combined with carbon monoxide. Unconsciousness takes place at about 50 per cent saturation and death may occur at a saturation between 65 and 80 per cent. Table 17 summarizes the symptoms at various stages of blood saturation.

TABLE 17

Symptoms of Carbon Monoxide Poisoning[13,14]

Percentage of blood saturation	Symptoms
0.0–10	None
10–20	Tightness across forehead, possibly headache
20–30	Headache, throbbing in temples
30–40	Severe headache, weakness, dizziness, dimness of vision, nausea and vomiting, and collapse
40–50	Same as previous item with more possibility of collapse and syncope, increased pulse and respiration
50–60	Syncope, increased respiration and pulse, coma with intermittent convulsions
60–70	Coma with intermittent convulsions, depressed heart action and respiration, possibly death
70–80	Weak pulse and slowed respiration, respiratory failure, and death

The symptoms decrease in number with the rate of saturation. If exposed to high concentrations, the victim may experience but few symptoms. The rate at which a man is overcome and the sequence in which the symptoms appear depend on several factors: the concentration of gas, the extent to which he is exerting himself, the state of his health and individual predisposition, and the temperature, humidity, and air movement to which he is exposed. Exercise, high temperature, and humidity, with little or no air movement, tend to increase respiration and heart rate and consequently result in more rapid absorption of carbon monoxide. The symptoms of chronic carbon monoxide poisoning are a tired feeling, headache, nausea, palpitation of the heart, and sometimes mental dullness.[15]

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[12] W. P. Yant, J. Chornyak, H. H. Schrenk, F. A. Patty, and R. R. Sayers, *U.S. Pub. Health Service, Bull. 211* (1934).

[13] R. R. Sayers and W. P. Yant, *U. S. Bur. Mines, Tech. Paper 373* (1925).

[14] R.R. Sayers and S. J. Davenport, *U. S. Pub. Health Service, Bull 195* (1937).

The above discussion shows that though carbon monoxide is not as poisonous a chemical as many others encountered in industry, it is still one of the most serious hazards. Four parts of carbon monoxide in 10,000 parts of air (400 parts per million) is considered the maximum concentration to which a person may be exposed for 1 hour without noticeable effects; or, if the concentration is increased from zero uniformly for 1 hour, the maximum concentration tolerable is 6 parts per 10,000 (600 parts per million), averaging 3 parts per 10,000 (300 parts per million) per hour.[16–18] The generally accepted maximum allowable concentration for daily 8-hour exposures is 100 parts per million.[19]

Large numbers of people die from carbon monoxide poisoning every year. In 1946 in New York City there were 268 suicide deaths and 281 accidental deaths from carbon monoxide poisoning alone. Of the latter, 254 were attributable to the accidental absorption of manufactured (illuminating) gas.

3. Classification of Methods for Detection and Determination of Carbon Monoxide

The methods for the detection and estimation of carbon monoxide in air are numerous. They may be placed into the following groups.

(1) Use of canaries and Japanese waltzing mice.

These small animals are more rapidly affected by carbon monoxide than are human beings.

(2) Absorption methods.[20]

(a) Ammoniacal or acid cuprous chloride.

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[15] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines, Miners' Circ. 33* (1938).

[16] Y. Henderson, H. W. Haggard, M. C. Teague, A. L. Prince, and R. M. Wunderlich, *J. Ind. Hyg., 3,* 72, 137 (1921).

[17] S. H. Katz, D. A. Reynolds, H. W. Frevert, and J. J. Bloomfield, *U. S. Bur. Mines, Tech. Paper 355* (1926).

[18] A. C. Fieldner, Y. Henderson, H. W. Haggard, A. L. Prince, and M. C. Teague, *U. S. Bur. Mines, Monograph 1* (1927).

[19] *Ind. Hyg. Newsletter, 7,* No. 8, 15 (1947).

[20] W. P. Yant and L. B. Berger, *U. S. Bur. Mines, Miners' Circ. 34* (1936).

(b) Cuprous sulfate-β-naphthol.

(c) Iodine pentoxide in oleum.[21]

Absorption methods are used for the relatively high percentages of carbon monoxide found in fuel gas, flue gas, etc., or in badly contaminated atmospheres. A known volume of the gas to be examined is shaken with one of the absorbents in a volumetric gas-analysis apparatus and the resulting decrease in volume is measured. Absorption methods are generally not practical when used for estimation of carbon monoxide present in less than 0.2 per cent quantity. Since this percentage is far above the toxic limits of carbon monoxide, absorption methods are of limited value from the standpoint of health and safety.

(3) Reduction methods.

(a) Reduction of palladious chloride.

(b) Reduction of ammoniacal silver nitrate.

These solutions react with carbon monoxide yielding, respectively, metallic palladium and silver.

(4) Oxidation methods.

(a) Hoolamite method.

This method depends upon the oxidation of carbon monoxide by an activated iodine pentoxide indicator. The amount of carbon monoxide present is shown by a color change produced by the coliberation of iodine from the iodine pentoxide.

(b) Iodine pentoxide method.

A known volume of air is passed through a tube containing iodine pentoxide at a temperature of 150° C. The liberated iodine is then trapped in potassium iodide solution and estimated by titration or the amount of carbon dioxide formed is ascertained.

(c) Red mercuric oxide method.[22]

The amount of carbon monoxide in air may be determined with the aid of the reaction:

$$\underset{\text{gas}}{CO} + \underset{\substack{\text{solid}\\\text{red}}}{HgO} \longrightarrow \underset{\text{gas}}{Hg} + \underset{\text{gas}}{CO_2}$$

The sample of air is passed through a reaction tube containing granular red mercuric oxide held at a temperature of 175–200° C. The loss in weight of the reaction tube is a measure of the quantity of carbon monoxide present.

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[21] G. Lunge and H. R. Ambler, *Technical Gas Analysis*, Van Nostrand, New York, 1934.

[22] J. D. McCullough, R. A. Crane, and A. O. Beckman, *Anal. Chem.*, 19, 999 (1947)

(5) Combustion methods.

(a) Platinum wire.

Any carbon monoxide present in a sample is burned on the surface of an electrically heated platinum wire. The heat developed by the exothermic reaction of forming carbon dioxide is then measured by some electrical device such as a Wheatstone bridge.[21]

(b) Hopcolite method.

Hopcalite is a catalyst which has the property of enabling carbon monoxide to be burned to carbon dioxide at ordinary temperatures. With a special apparatus the concentration of carbon monoxide may be read directly from the dial of a milliammeter registering the heat evolved and calibrated to read parts per million of carbon monoxide.

(6) Colorimetric methods.

(a) Chemical.

These methods may also be considered as part of category (3) reduction methods above.

1. NBS indicating gel.

Purified silica gel impregnated with ammonium molybdate, and a sulfuric acid solution of palladium or palladium oxide, forming a yellow silicomolybdate, is reduced to a molybdenum blue by carbon monoxide, the reaction being catalyzed by the palladium.

2. Palladium chloride-phosphomolybdic acid-acetone reagent.

In this method too, developed by the U. S. Bureau of Mines, a molybdenum blue is formed, the depth of color being proportional to the amount of carbon monoxide drawn through the test solution.

(b) Biochemical.

Carbon monoxide forms carboxyhemoglobin, a characteristically colored compound with the hemoglobin of blood. When diluted, normal blood has a yellow color but when blood containing carbon monoxide is diluted it has a pink color. These methods are based on estimating the amount of carbon monoxide by the amount of color attributable to the carboxyhemoglobin.

1. Pyrotannic acid method.

Treatment of a diluted blood sample with tannic and pyrogallic acids yields a gray-brown suspension with normal blood and a light carmine suspension with blood containing carboxyhemoglobin.[23-25]

2. Haldane carmine method.[26]

This method depends on the amount of carmine, a dye solution to be added to diluted blood to yield the same color as blood completely saturated with carbon and at the same time noting the amount of carmine solution to be added to diluted normal blood to give it the color of the blood with the unknown content of carbon monoxide. The ratio of these additions gives a measure of the blood saturation.

(7) Blood methods.

These methods cannot be used for the estimation of the quantity of carbon monoxide in air, for the amount of carbon monoxide hemoglobin in a person's blood is a factor depending on so many variables that no exact relationship can be derived.

(a) Spectrophotometric methods.[27]

These methods are based on the fact that carboxyhemoglobin will absorb light of certain wave lengths different from the absorbed by oxyhemoglobin. Any mixture of these two substances will absorb light as some function of the concentrations of both substances. With blood containing carbon monoxide hemoglobin, the absorption band will be slightly nearer the violet end of the spectrum and in addition the extent of this difference in wave length is related to the percentage of blood saturation. To enable one to measure this difference more accurately the effect can be doubled by the simple expedient of employing two spectra in reverse directions with the aid of a revision spectroscope. This is necessary because the absorption bands of carboxyhemoglobin and oxyhemoglobin lie close together. The large differences in the spectra of oxyhemoglobin and carboxyhemoglobin in the near infrared region have provided a method for the determination of carbon monoxide.[27a]

(b) Volumetric method.[28,28a]

Oxygen and carbon monoxide are freed from hemoglobin by potassium

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[23] R. R. Sayers and W. P. Yant, *U. S. Pub. Health Service, Reprint 790* (1922).

[24] R. R. Sayers, W. P. Yant, and G. W. Jones, *U. S. Pub. Health Service, Reprint 872* (1924).

[25] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines, Miners' Circ. 33* (1938).

[26] C. G. Douglas and J. S. Haldane, *J. Physiol. 44*, 305 (1912).

[27] R. C. Frederick, *Analyst, 56*, 561 (1931); *62*, 452 (1937).

[27a] B. L. Horecker and F. S. Brackett, *J. Biol. Chem., 152*, 699 (1944).

[28] D. D. Van Slyke, *J. Biol. Chem., 40*, 104 (1919); *49*, 1 (1921); *61*, 523 (1924); *72*, 39 (1927); *73*, 121 (1927); *95*, 509 (1932).

[28a] P. F. Scholander and F. J. W. Roughton, *J. Ind. Hyg. Toxicol., 24*, 218 (1942)

ferricyanide. The gases are then removed by a vacuum in a Van Slyke apparatus, the oxygen is absorbed by alkaline pyrogallate, and the volume of the residual carbon monoxide is measured directly at atmospheric pressure.

4. Detection

a. Canaries and Japanese Waltzing Mice

Small birds such as canaries may be used to detect carbon monoxide. Generally they will exhibit signs of distress and fall from their perch before sufficient carbon monoxide is present to affect a man. It has been shown that a man may feel only a slight headache at the end of 20 minutes in an atmosphere containing 0.25 per cent carbon monoxide, while canaries will show signs of distress in 1 minute and fall from their perch within 3 minutes.[29]

The United States Bureau of Mines[30] has shown that Japanese waltzing mice are equally as susceptible to carbon monoxide as canaries. They are black and white in color, with an average body length of 72 mm., tail length 52 mm., and weight 17 g. They appear to be unable to orient themselves in a horizontal plane. As a result they run erratically, sometimes in circles and sometimes in wide, narrow, or figure-eight forms, repeated many times in rapid succession. At other times they pivot on one foot and make many gyroscopic circles without stopping. They are totally deaf, this condition being probably due to the same morphological or physiological cause as that of the peculiar running movement. The effect of a small fraction of 1 per cent of carbon monoxide on the mice is to quiet their movements immediately. Waltzing mice are more sensitive to lower percentages of carbon monoxide than canaries, for waltzing mice exposed to 0.10 to 0.12 per cent carbon monoxide gave positive indication of carbon monoxide poisoning after 5 to 10 minutes, whereas canaries failed to give such indication after 75 to 131 minutes.

These small animals are comparatively widely used as carbon monoxide detectors, especially in coal mines. It is to be noted that although Japanese waltzing mice appear to be slightly more sensitive to atmospheres deficient in oxygen and to the presence of carbon monoxide than canaries and the latter are more sensitive than man, the margin of time between serious response of man and observable response of these animals is not wide enough in most instances for either canaries or waltzing mice to be of really practical use for avoiding harmful exposure of man.[30]

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[29] *Fed. Bd. Vocational Education, Bull. 39, Coal-Mine Gases* (1931).

[30] W. P. Yant, F. A. Patty, H. H. Schrenk, and L. B. Berger, *U. S. Bur. Mines, Rept. Invest. 3040* (1930).

b. Palladious Chloride Detector

There are many variations of this detector. One of the simplest is an ampoule type of carbon monoxide detector. It was devised primarily for examining the air of manholes and sewers for possible dangerous contamination with carbon monoxide before workmen enter these places. It may also be used for examination of atmospheres that are known to be contaminated with carbon monoxide, as the air in garages, tunnels, mines, around blast furnaces, gas plants, and even in the home. The NBS carbon monoxide indicating tubes described below are better.

Ampoules. The detector consists of an absorbent-cotton-covered, easily crushed, glass ampoule, which is filled with a palladious chloride solution that changes color when exposed to carbon monoxide and a color chart. The procedure is to crush the ampoule, which in turn wets the absorbent-cotton covering with palladium chloride solution. Expose it to the air to be tested. If carbon monoxide is present it will react with the palladious chloride and change the color of the ampoule from the brownish-yellow stain of the solution to varying degrees of yellowish black to black, depending on the concentration of carbon monoxide.

The chemical reaction involved is, as was explained above, a reduction of the palladious chloride by carbon momoxide to form a finely divided black precipitate of metallic palladium, while the carbon monoxide is oxidized to carbon dioxide. The finely divided precipitate of metallic palladium, which in appearance is much like carbon black, is deposited in the cotton fiber. The detector gives semiquantitative indications of carbon monoxide in a range of concentrations of 2 to 10 parts per 10,000 parts of air by volume when the temperature of the air is above 10° C., or 50° F. The sensitivity of the detector decreases with low air temperatures and a longer period of exposure than the prescribed 10 minutes is required to give a satisfactory indication of the amount of carbon monoxide present; 20 to 30 minutes is required for temperatures between 50 and 32° F.

It has been shown[31] that gasoline vapor, ethylene, hydrogen, and hydrogen sulfide produced a change in the color of the ampoules similar to that caused by carbon monoxide.[32,33] Concentrations of these gases which produced the change, however, were also dangerous because of a hazard of either poisoning or explosion.

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[31] L. B. Berger and W. P. Yant, *U. S. Bur. Mines, Rept. Invest. 3030* (1930).

[32] R. R. Sayers and S. J. Davenport, *U. S. Pub. Health Service, Bull. 195* (1937)

[33] U. S. Patent 1644014.

Test Papers.[34] Another variation of this method is a device which consists essentially of a sheet of dry paper impregnated with a 2 per cent solution of palladious chloride and a sheet of plain paper held together between two plates of glass. The device is suspended in the suspected atmosphere for a definite time and in the presence of carbon monoxide the sensitized paper uniformly turns gray. Illuminating gas acts the same way, of course. Hydrogen sulfide produces a blackish-brown coloration but only along the edges of the paper. The test can be made roughly quantitative by making the unsensitized paper into a series of panels of colors corresponding to increasing carbon monoxide contents and cutting a circle out of each panel, through which the sensitized paper can be observed, so that the color produced on the sensitized paper can be compared directly with those of the various panels.

Still other variations of this test designed to increase its accuracy are described by Winkler.[35]

The official British[36] method for the detection of carbon monoxide by means of palladious chloride uses the following procedure:

Apparatus. The atmosphere being tested is sampled by means of the apparatus shown in Fig. 93. A 5-liter aspirator (A) is fitted with a device to control the rate of flow. The air sample is drawn through a test paper clamped in a holder (Fig. 13), the holder being screwed into the stopper of the aspirator. A glass extension tube (D) fits into the lower part of the stopper and extends almost to the bottom of the aspirator; its lower end must always be below the surface of the water. In this way a constant head of water is maintained and the flow from the aspirator remains constant. The depth from the lower end (X) of the glass tube to the end of the outlet tube (Y) should be at least 18 inches. A drying tube, approximately 6 inches by 1-inch bore, filled with activated charcoal, 12- to 18-mesh, fits by means of a rubber stopper into the inlet of the paper holder, so that its lower end is as far as possible above the test paper. Small pieces of fine wire gauze keep the charcoal in position, and the tube is closed at the top by a bored rubber stopper. Care must be taken to free the drying tube and activated charcoal from charcoal fines. The charcoal must be renewed after about 250 tests.

Preparation of Test Papers. Prepare the palladium chloride solution as follows: Boil 0.1 g. of pure palladious chloride for a few minutes in 20 ml. of water. Filter the mixture, cool the filtrate, and make up to exactly 20 ml. with water. Add 20 ml. of acetone and stir the mixture. Keep the solution in well-stoppered hard-glass bottles that have been thoroughly washed, first with acid and then with water. No deterioration should normally take place. If, however, at any time the solution becomes cloudy, with the formation of an orange deposit, a fresh reagent solution must be prepared.

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[34] E. Chaignon, *15me Congr. chim. ind., 1936,* 261; *Chem. Abstracts, 30,* 5464 (1936).

[35] L. W. Winkler, *Z. anal. Chem.,* 102, 99 (1935); *Chem. Abstracts, 29,* 3626, 7222 (1935).

[36] *Dept. Sci. Ind. Research Brit., Leaflet 7* (1939).

Prepare the test papers from Postlip No. 633 extra-thick white filter paper (18 × 24, 60 pound) or equivalent filter paper, cut into strips 2 inches wide. Immerse the strips in the palladious chloride reagent solution for 1 minute. Allow to drain for a few seconds and then remove the superfluous liquid by pressing *very lightly* between filter paper. Cut off 1 inch at the top and bottom of each strip and cut the remainder into 3-inch lengths. The papers must be prepared immediately before use.

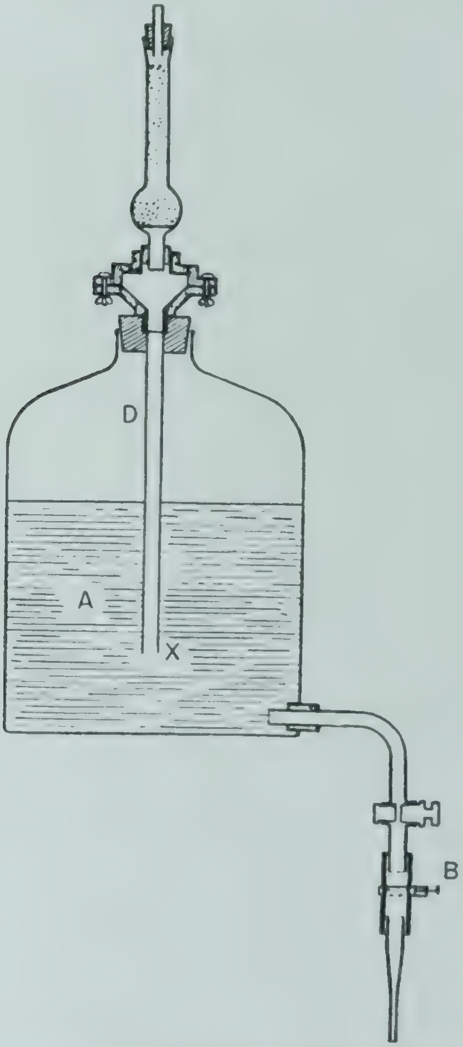

Fig. 93. Apparatus for the detection of carbon monoxide.

Procedure. Fill the aspirator with water and adjust so that it will give a flow of 50 ml. per minute. This rate need not be exact but should be within the range of 45–55 ml. per minute. Insert the test paper prepared as directed above into the holder and clamp firmly by tightening the wing nuts.

To obtain an approximate estimate of the carbon monoxide concentration, open the tap of the aspirator and start a stop watch. After the first 2 minutes, stop the flow and examine the test paper. If only a slight stain is obtained, continue the test, examining the test paper every 5 minutes, until a stain is obtained slightly deeper than the first standard stain but lighter than the second standard stain. The total sampling time from the beginning of the test is noted and the corresponding concentration is obtained from a chart accompanying the standard stains.

c. NBS Indicator

The National Bureau of Standards carbon monoxide indicator[36a] is based on preliminary work done by the Royal Aircraft Establishment, Farnborough, England. The discovery by the National Bureau of Standards investigators of the necessity for the elimination of all traces of chlorides and organic matter in the indicating gel was the basis of a significant advance in the development of detector methods for carbon monoxide.

When highly purified silica gel, impregnated with ammonium molybdate, and a solution of palladium or palladium oxide digested in sulfuric acid, is exposed to carbon monoxide, a molybdenum blue is formed, the depth of color varying from faint green to blue in proportion to the amount of carbon monoxide.

Preparation of the Indicating and Guard Gels. As mentioned, traces of chlorides or organic matter will spoil the indicating gel, therefore all glassware must be carefully cleaned, preferably with fuming sulfuric acid.

Purification of the Silica Gel.[36b]—Gels No. 697535-600-C and No. 69520-650 should be free from bits of wood, paper, or other foreign matter. The gels must be purified by oxidation with nitric acid as follows:

Place approximately 3.2 pounds of gel into a 4-liter Pyrex serum bottle, cover 2 inches with nitric acid (sp. gr. 1.42), and immerse the bottle to its upper shoulder in a steam bath. Digest for one week, during which time the level of the acid should be maintained, and keep a free flow of steam stirring through the bath. A ₮ 45/50 male grinding should be drawn into a retort-shaped delivery tube and inserted in the corresponding grinding of the bottle neck to discharge condensate into a beaker; or a reflux condenser can be used.

Remove the acid by means of an immersion filter attached to a trap and suction. A satisfactory filter is made from a 25-mm. porcelain plate with 1-mm. holes, sealed loosely into an 18- by 22-mm. Pyrex tube. Smaller holes tend to plug. In removing acid or water from the gel, try to avoid producing a water hammer with the suction.

[36a] Martin Shepherd, *Anal. Chem.*, *19*, 77 (1947).

[36b] Use Davison Chemical Corporation (Baltimore, Md.) No. 697535-600-C silica gel for the preparation of the indicating gel and their No. 69520-650 for the guard gel.

Wash the gel with distilled water according to the following schedule, and replace in the steam bath after each complete washing:

Time after removal of acid, days	Complete changes of water, with removal of water between each change
0	12
1	7
2	5
3	3
4	2

The pH of the wash water after a final 2 days' leaching in the steam bath should be 5.0 or greater for the No. 697535-600-C gel, and 4.9 or greater for the No. 69520-650 gel. Continue washing if necessary to achieve this condition. When proper pH is reached, remove water thoroughly with the immersion filter, place the bottle in an electric oven at 100° C. until gel appears dry, and then heat 3 days at 320° C. In the same oven place a tube containing guard gel. This tube is made from a ₮ 45/50 male grinding extended 5 cm. at the small end and then closed except for twenty 1-mm. holes. The large end is rounded and drawn down to a 1-cm. ringed neck, which may be grasped with crucible tongs. The whole tube is filled with guard gel previously prepared. After 3 days, remove the bottle of activated gel and immediately insert the guard tube. When the gel is cool, it is ready for use.

Guard Gel.—The No. 69520-650 gel needs no further treatment other than the purification given above. It is the guard gel used to protect the indicating gel in the final indicating tube. It must be kept dry and free from organic vapors and must therefore be stored in ₮ 45 bottles equipped with guard tubes, which are themselves filled with guard gel.

Indicating Gel.—After purification and activation, the No. 697535-600-C gel is converted into indicating gel by impregnating with a palladium and molybdenum solution, followed by drying in two successive stages.

Reagents. Palladium Sulfate Solution.—Heat about 14 g. of finely divided palladium metal at 600° C. overnight in a furnace to convert as much as possible to palladium oxide, PdO. Transfer this to a 500-ml. Pyrex boiling flask having a thermometer well and a ₮ joint, add 175 ml. of concentrated sulfuric acid, connect a reflux condenser, and heat to boiling (about 300° C.) until all of the palladium and its oxide appear to have been converted to sulfate. At this point, a dark-brown, shiny, crystalline precipitate will be formed. Continue heating, and add water slowly and cautiously, not more than 1 ml. at a time, through the top of the condenser. If sulfur dioxide is evolved, as evidenced by its odor, stop adding water and heat at the then existing temperature until no more sulfur dioxide is evolved. Then slowly continue the addition of water, stopping the refluxing if necessary, until all of the crystalline precipitate has dissolved and the boiling temperature is 200° C. Cool the solution, filter through a porous porcelain or glass filtering crucible of fine porosity, and dilute to 500 ml. in a volumetric flask.

Dilute a 5-ml. aliquot of this solution to 250 ml. and determine the palladium content by precipitation with dimethylglyoxime[36c] and the sulfuric acid content by titrating the filtrate and washings from the palladium precipitation with standard alkali, using methyl red as the indicator. Calculate the amount of additional sulfuric acid needed and the volume to which the solution must be diluted to give a final solution containing 0.013 g. of palladium and 0.33 g. of sulfuric acid per ml.

Molybdenum Solution.—Dissolve 50 g. of reagent-quality ammonium molybdate in 1 liter of water.

Impregnating the Gel.—Mix 750 ml. of water, 450 ml. of ammonium molybdate solution, and 100 ml. of palladium sulfate solution in a clean 4-liter Pyrex serum bottle. Slowly add to this 2 liters of the purified, freshly activated silica gel, rotating the bottle so that the gel is always submerged. The bright yellow silicomolybdate complex forms immediately. Allow to stand 2 hours or overnight.

Initial Drying.—Heat the bottle of impregnated gel to 60° C. in a water bath, reduce the pressure in the bottle to about 4 cm. of mercury, and evaporate off the excess water. During this process remove the bottle from the water bath every minute or two and tap it firmly on a sponge rubber pad in such a way that the solid which tends to coat out on the walls of the bottle is continually moistened and taken up by the gel. When the gel is surface dry, continue to heat and evacuate, rotating the bottle vigorously in the water bath every 2 or 3 minutes. At first, when a fresh portion of the surface-dry gel comes in contact with the hot wall of the bottle, the evolution of water vapor is evidenced by the quivering and dancing of the gel. When this finally ceases, the initial drying is completed. The gel has now turned from pale to bright yellow. The time required for this process is about 6 hours.

To reduce the pressure in the bottle for the above process, first connect it to an adapter made from a ₮ 45/50 male grinding drawn out to a 10-mm. tube pointing downward. This grinding should fit the corresponding female one in the neck of the bottle well enough so that when water is used as a lubricant no excessive leakage occurs at 4 cm. absolute. About two-thirds of the bottles and grindings taken from the stock should meet this requirement. Never lubricate this grinding with anything but water. It will operate satisfactorily dry during the last stages of drying. Connect the adapter to a 2-liter filter flask, and this in turn to an efficient water aspirator. A mercury manometer may be teed into the line to indicate proper operation of the aspirator. A 25-pound lard can can serve as the water bath, and a rubber tube tied between its handles keeps the bottle submerged to the proper level between the periodic shakings.

Final Drying.—Transfer equal portions of the partially dried indicating gel to fourteen 500-ml. round-bottom boiling flasks having necks 35 cm. long and 2.5 cm. bore, which terminate in a ₮ 24/40 grinding. This transfer is facilitated by an adapter made from a ₮ 45/50 male grinding, drawn down and curved like a spout. Connect these flasks to a manifold having a series of ₮ 24/40 female grindings sealed as tees to a horizontal tube, which in turn connects through a trap immersed in liquid air to a McLeod gauge, a mercury-vapor pump, and a mechanical backing pump.

[36c] R. Gildchrist and E. Wichers, *J. Am. Chem. Soc.*, *57*, 2565 (1935).

The cold trap should accommodate about 50 g. of ice without plugging.[36d] Evacuate the system until the pressure has dropped to approximately 0.028 mm. This will probably vary some with each apparatus. The time required is about 20 hours.

Shut off the pump, gauge, and trap, and slowly open the flasks to the atmosphere through a large drier containing alternate layers of silica gel, Hopcalite, and silica gel. When atmospheric pressure is reached, remove the flasks, very carefully remove grease from the male grindings, using only a dry, clean cloth, and transfer the dried gel back into the serum bottle, closing this with a dry ₸ 45 stopper. Determine the water content of the gel as detailed below.

Determination of Water Content, Optimum Water Content, and Blending. Make an empirical test as follows: Weigh out 1 to 2 g. of the gel in a conical glass-stoppered weighing bottle, place this in a small Pyrex vacuum desiccator containing purified and activated silica gel, and put this in turn in a vacuum electric oven at 105° C. for 16 hours while continuously evacuating. Admit air to the cooling desiccator through a drying tube, and weigh the cooled bottle to determine the loss in weight. It is recognized that this test is not a true determination of water, since all of the water is not driven off, and some of the acid probably is. However, it is sufficient for controlling the preparation of the gel.

The sensitivity of the gel is a function of its residual water content, and while gels are sensitive over a fairly wide range—about 2 to 20 mg./g.—the optimum lies between 8 and 12 mg./g. For immediate use in laboratory-type tubes (see below) against dry silica gel, reduce the water to 10 or 12 mg./g. For field use after storage for 1 month or longer in sealed tubes against dry gel, reduce the water to 15 or 16 mg./g.

If the drying process yields gels with less water than corresponds to the optimum, blend these with gels containing more water than the optimum. Blend by mixing *thoroughly* in 4- or 9-liter serum bottles in the proper proportion by weight (or volume) to produce the desired total water content per gram. The water content of the wet gel should not exceed 100 mg./g.; and the dry gel should contain no less than 2 mg./g. Allow 1 month's storage to secure equilibrium.

Blending is not necessary if a product of uniform calibration is not required. Thus in the laboratory determinations may be made with color standards prepared from indicating tubes, and the same gel used for the unknowns. But matching to a definitely set series of colors in the field requires a gel of uniform sensitivity.

Preparation of the Indicating Tubes. Laboratory Tubes.—These are for immediate use for accurate determinations. They are capable of yielding values within 0.0002 per cent by volume in the range 0–0.01 per cent carbon monoxide. These tubes cannot be stored longer than 8 hours. The indicating gel need not be adjusted to a standard sensitivity as long as one lot of gel is used to make the color standards and tests of the unknowns.

Use 7-mm. clear Pyrex glass tubing without noticeable color. Cut into 15-cm. lengths and fire polish. Clean with fuming sulfuric acid, or by heating at 550° C. for 1 hour, or select freshly drawn tubing which has been carefully protected from dirt. Plug a 000 cork in one end, insert loosely a small pad of absorbent cotton, and then fill alternately and in order with 4 cm. of guard gel, 15 mm. of indicating gel, and 3 cm. of guard gel. Insert a second cotton pad and tamp loosely to hold the gel in place, then close with a second 000 cork.

[36d] Apiezon L may be used to lubricate ₸ joints and stopcocks in this vacuum system, but the pumps must be started imediately after the flasks are connected and some positive flow from the gel to the trap and pump must be maintained hereafter.

Glass-stoppered pear-shaped separatory funnels with dry ₮ 4 stopcocks make convenient gel venders. A system of dosing stopcocks may be made from ₮ 19/22 male joints sealed to ₮ 4 stopcocks. The ₮ 19/22 joint plugs into a ₮ 19 reagent bottle which holds the gel. Two stopcocks can be spaced to form a pocket of the proper size for a dose of guard gel. A solid ₮ 4 stopper can be drilled with a pocket of proper size to hold a dose of the indicating gel.

The day's supply of laboratory tubes may be stored in a desiccator over guard gel.

NBS Indicating Tubes for Field Use.—These tubes are used for the rapid determination of any physiologically significant amount of carbon monoxide. The colors developed are matched against painted chips, and the indicating gel must accordingly be adjusted to a standard sensitivity.

Use the same size tube, but for convenience cut 23-cm. lengths. Clean and fire polish as above. Draw down one end of the tube to a tip 1 cm. long and 1 to 1.5 mm. outside diameter. The length from the rounded shoulder to the end of this tip should be nearly 15 mm. Heat in an electric oven to expel any condensed water.

Insert a rectangular piece of 1- by 0.007-inch Fiberglas tape No. ECC1B, cut 1 by $^7/_{16}$ inch, which was previously cleaned by heating in an electric furnace to 550° C. for 2 hours. Tamp this firmly into the sealed end with a clean 4.5-mm. steel drill rod.

Fill the tubes with alternate layers of guard and indicating gel as follows: 4.5 cm. of guard gel, 14 mm. of indicating gel, and 2.5 cm. of guard gel. Insert a second Fiberglas plug and tamp firmly against the gel. Tap down the gel thoroughly by vibrating the tube held vertically. Tamp down the glass plug a second time. Seal off the tube 2 cm. or more away from the gel, drawing into a second tip like the first.

In handling large batches of tubes, large desiccators containing a layer of guard gel offer satisfactory temporary storage. However, the tube should be sealed within 1 hour after filling. The room where this work is done should be free from carbon monoxide, organic vapors, reducing or oxidizing gases such as ethylene, acetylene, and hydrogen sulfide, or ozone, and nitrogen peroxide. The humidity should not be excessive, and air conditioning is helpful.

If a glass-sealing machine is used proper mechanical adjustment will always keep the tip of the flame away from an open end of the tube. In sealing off by hand this must carefully be avoided, for the carbon monoxide generated in the partial combustion caused by contact of flame with cold glass will usually ruin the indicating tube.

If the indicating tube is properly prepared it should remain useful for several years.

Colorimetric Determination. As has been stated, the color response of the indicating gel is a function of time times concentration at any constant rate of flow, and most of the analytical methods used or proposed have taken advantage of this fact. A fairly close estimation of the concentration of carbon monoxide in an unknown may be made by simply measuring the time (at constant flow) necessary to produce a standard color. A more accurate determination can be made by matching an unknown with a set of standard colors produced by exposing the tubes themselves to known concentrations.

Interfering substances can be strong reducing or oxidizing gases or vapors which are present in amounts sufficiently large to escape the inlet guard gel. The field tubes were made to remove any interfering substances ordinarily present in any of the atmospheres associated with military equipment or installations, and are probably good for any ordinary industrial or household use. However, this should be checked in special cases. The indicating gel has so little sensitivity toward hydrogen that its presence in large amounts does not interfere with determinations of carbon monoxide.

It is possible to modify the indicating tube so that it will serve to detect and estimate the presence of other reducing or oxidizing gases. Hopcalite can serve to remove any carbon monoxide present, and an anhydrous calcium sulfate can be substituted for the guarding silica gel. This combination will detect many organic vapors or unsaturated gases. The oxidation of a previously reduced tube is also possible.

Laboratory Method. Air to be tested is passed through a NBS indicating tube (laboratory type) at 90 ml./min. for a definite period. The color obtained is compared with freshly prepared standards of carbon monoxide. In the range 0 to 0.01 per cent by volume, carbon monoxide can be determined with a reproducibility of 0.0002 per cent and a probable accuracy of 0.001 per cent or better. Above 0.01 per cent, the sample may be diluted with a known proportion of carbon monoxide-free air if sufficient differentiation of the darker colors proves difficult.

Apparatus. One calibrated flowmeter registering 90 ml./min.; two or three additional flowmeters for diluting the sample in known proportions with carbon monoxide-free air; one stop watch; standard mixtures of carbon monoxide in air under pressure; and laboratory-type indicating tubes.

Procedure. Pass sample to be tested through a freshly prepared indicating tube at a measured rate of 90 ml./min. Note time in seconds required to approximately match the color developed by exposure to 0.005 per cent carbon monoxide for 50 seconds, an easy color to match. The composition of the unknown can now be approximately computed. *Example:* Unknown developed the "0.005 per cent, 50-second color" in 95 seconds. Concentration of unknown was therefore $50/95 \times 0.005 = 0.0026$ (approximately).

Now prepare a set of color standards from freshly filled indicating tubes and the 0.005 per cent standard mixture, using the knowledge derived above in order to bracket the unknown with lighter and darker colors, and taking the nearest 10-second interval as the exposure time for the unknown. To continue the example given above: Exposure time for unknown is conveniently selected as 100 seconds. Since it is approximately 0.0025 per cent, to bracket it would require exposure of 0.005 per cent for 50 seconds as a base time, with greater and lesser exposures. With 0.005 per cent for 50 seconds as a base, each 1-second difference would correspond to 0.0001 per cent carbon monoxide. If tubes were then exposed to this concentration for 46, 48, 50, 52, and 54 seconds, this standard set would represent the percentages 0.0046, 0.0048, 0.0050, 0.0052, and 0.0054, respectively, on the 50-second base, but one-half these amounts on the 100-second base: 0.0023, 0.0024, 0.0025, 0.0026, and 0.0027. The unknown, exposed for 100 seconds, is now compared with this standard set. Suppose its color lies between the 52- and 54-second tube, or between 0.0026 and 0.0027 per cent. It would be reported as 0.00265 per cent ± 0.00005. During the determination of the order of the color intensity of these tubes, the identifying labels should be obscured. If the observer then arranges the color *standards* in their proper order, he has proved his analysis. Often differences in color are not apparent at first glance but resolve upon close comparison. North or sky light or a daylight fluorescent lamp is recommended for this work.

In actual practice, if the accuracy indicated above is to be realized, the standard color tubes should have been prepared from a mixture containing 0.0025 per cent carbon monoxide in air. The color developed is practically, but not *exactly*, determined by concentration of carbon monoxide times duration of exposure. If an exposed tube is immediately flushed with carbon monoxide-free air, thus removing unreacted residual carbon monoxide, the expressed relation is more nearly exact. If a 0.005 per cent standard is used to make color tubes for determinations in the range 0 to 0.01 per cent, a reproducibility of 0.0002 per cent and an accuracy of 0.0001 per cent or better are easily achieved, however.

As the concentration of carbon monoxide increases, the colors developed become darker and more difficult to match. Reduction of the exposure time with some loss in reproducibility and accuracy will serve for a while; but above 0.02 per cent dilution is comforting, and with increasing concentrations, is finally necessary.

Field Method. A 2-ounce aspirator bulb equipped with a rate-controlling valve is adequate. It is cheap, readily available, and apparently can be used successfully by anyone. The tubes and an aspirator bulb equipped with a color chart are commercially available.

d. Hoolamite Detector

Hoolamite, $I_2O_5 + H_2SO_4 + SO_3$, activated iodine pentoxide, named after Hoover and Lamb,[37] who patented the formula, is a mixture of iodine pentoxide and fuming sulfuric acid on granular pumice stone. When carbon monoxide comes in contact with this reagent, iodine is liberated, changing the originally white granules to bluish green of increasing depths, then violet brown, and finally black, depending upon the concentration of carbon monoxide. The chemical reaction that liberates the iodine is:

$$I_2O_5 + 5CO \longrightarrow 5CO_2 + I_2$$

Hoolamite averages approximately 12.29 per cent of iodine pentoxide, 51.89 per cent of sulfuric acid (47 per cent sulfur trioxide, SO_3), and 35.82 per cent of pumice granules. As moisture causes deterioration of Hoolamite, it is marketed in small glass ampoules tapered at both ends and hermetically sealed.

The Hoolamite indicator for carbon monoxide was used by engineers of the U. S. Bureau of Mines and others engaged in rescue and recovery operations, such as men engaged in fighting mine fires or performing mine rescue work. This detector largely replaced the use of canaries and mice, as it required less care and attention under most conditions and is more accurate.[38]

The complete indicator comprises a metal barrel filled with activated charcoal, through which air is drawn by means of a rubber aspirator. The inlet end of the barrel has a corrugated tip, to which an extension sampling line may be attached. The air is then discharged by the aspirator through a small glass tube containing Hoolamite. A comparison color tube having five permanent colors in pumice stone, graduated from 0.10 to 1.0 per cent of carbon monoxide, is placed alongside the Hoolamite tube. The scale and tube are kept in position by holders firmly attached to the metal barrel.

Another type of this detector consists of a short metal barrel having a corrugated tip, containing the inlet opening and valve, a rubber aspirator, another short barrel containing the outlet valve, a metal tube connecting the outlet valve barrel to a larger barrel containing activated charcoal, a Hoolamite tube, a color tube, a tube holder, and a metal strip connecting the charcoal barrel and the inlet valve barrel. Air entering the rubber bulb by way of the inlet opening and valve is discharged when the bulb is depressed through the outlet valve, thence through the small metal tube, and through the activated charcoal into the Hoolamite tube. A comparison color tube for the aforementioned percentages of carbon monoxide is held in place by placing one end of the tube in a small depression on the tube holder and by slipping a spring fastener over the other end. The Hoolamite tube is held in place in a similar manner, except that the bottom end of the tube is inserted into an opening having a rubber tube that serves as a gasket. The tip of the inlet valve is also equipped with a corrugated tip to which an extension sampling line may be attached. The location of the valves and the ease with which they may be removed and cleaned or repaired makes this type of detector preferable to the former type.

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[37] A. B. Lamb and C. R. Hoover, U. S. Patent 1321062 (1919).

[38] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines, Miners' Circ. 33* (1938).

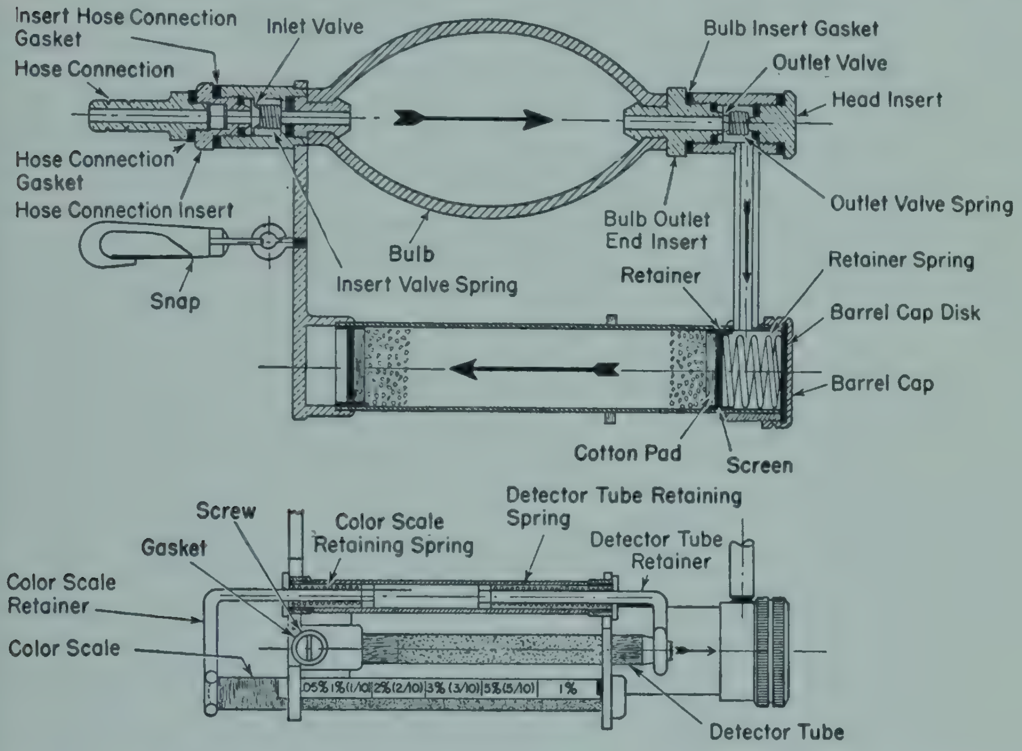
Insert Hose Connection Gasket
Inlet Valve
Bulb Insert Gasket
Outlet Valve
Head Insert
Hose Connection
Hose Connection Gasket
Hose Connection Insert
Outlet Valve Spring
Bulb Outlet End Insert
Bulb
Retainer
Retainer Spring
Insert Valve Spring
Snap
Barrel Cap Disk
Barrel Cap
Cotton Pad
Screen
Detector Tube Retaining Spring
Screw
Color Scale Retaining Spring
Detector Tube Retainer
Gasket
Color Scale Retainer
Color Scale
.05% 1%(1/10) 2%(2/10) 3% (3/10) 5%(5/10) 1%
Detector Tube

Fig. 94. Cross section of carbon monoxide detector (arrows show course of air sample). (*Courtesy Mine Safety Appliances Co.*)

Before either type of Hoolamite detector is taken into an atmosphere to be inspected the aspirator bulb should be carefully tested to see if it works, that it does not leak and has the proper resilience; that the valves of the detector are tight and function properly; that the color tube is held securely in place; and that the activated charcoal is in good condition. If the material in the Hoolamite tube becomes discolored when squeezed 20 times in pure air the charcoal container should be refilled with fresh activated charcoal. In reassembling the instrument care should be taken to replace the spring that holds the charcoal in place correctly, otherwise air channels through the charcoal might result.

Procedure. If no extension sampling line is used, the operator of the detector should be protected by a suitable respiratory apparatus when working in an atmosphere liable to contain carbon monoxide.

Squeeze the bulb once or twice to remove any moisture and to fill the instrument with air identical with that to be tested. Break both tips of a Hoolamite tube and insert it firmly in the instrument with the shoulder securely seated in the rubber connecting joint. Squeeze the bulb 10 times in succession, collapsing it completely each time. This will force about 350 ml. of air through the impregnated pumice. A slight amount of smoke or fume should issue from the Hoolamite tube when the bulb is squeezed. Although this smoke is harmful if breathed directly, under ordinary conditions it will be diluted so quickly by the surrounding air that no symptoms other than coughing are likely to be noted if no respirator is worn. Observation of the smoke, however, is often advantageous as indicating the direction and velocity of the ventilating current of the surrounding atmosphere.

After squeezing the aspirator the full number of times, compare the resulting color, if any, with the permanent colors in the color tube and note the corresponding percentage of carbon monoxide. At low concentrations of carbon monoxide the color in the Hoolamite tube fades rapidly, hence the comparison with the color tube should be made at once. If no color comparable with those in the color tube results from 10 squeezes, repeat the test, using some multiple of 10, and make the corresponding correction in the percentage indicated by the color obtained. For instance, if a color corresponding to that for 0.1 per cent is obtained with 20 successive squeezes, the amount of carbon monoxide in the air samples is about 0.05 per cent; or, if a color corresponding to that for 1.0 per cent is obtained with 5 squeezes, approximately 2 per cent of carbon monoxide is indicated in the air being sampled. As stated, the operator should be protected by a respiratory device capable of protection against carbon monoxide while working in an atmosphere suspected of containing that poison.

Remove the Hoolamite tube from the instrument promptly, as it should not be left in place longer than the time necessary to make the test. If the color in the tube does not fade or if a yellow discoloration appears, the tube should be discarded. As the iodine pentoxide mixture is highly acid, a discarded tube should not be thrown where it can do any damage. If the tube is to be used again, the tips should be covered with rubber caps, like those used for serum ampoules, to prevent the deterioration of the contents through entrance of moisture.

If an extension line is attached to the corrugated tip of the barrel and the other end of the sampling line is connected with a pipe leading through a stopping of a sealed area in a mine, or extends to an inaccessible place, the percentage of carbon monoxide in the air of the immediate region behind the seal or in the inaccessible place may be ascertained, provided the pipe in the stopping is not intaking or provided the stopping is not leaking. Furthermore, the line to the inaccessible place must be properly purged first with the air or atmosphere to be sampled before it is connected to the corrugated tip. Determinations of this sort are particularly useful during the work of fighting mine fires.

The detector does not indicate a deficiency of oxygen or the presence of such other gases as carbon dioxide or hydrogen sulfide in the atmosphere being tested, nor does it automatically give warning of the presence of carbon monoxide. The operator may actually be in an atmosphere containing this gas while using the instrument without knowledge of its presence. Hence, in these respects, the detector is inferior to canaries or Japanese waltzing mice. However, when in good condition and used in the manner described above, the detector affords a reasonably accurate quantitative means of determining carbon monoxide.

Although the iodine pentoxide indicator is used more or less generally, it should not be forgotten that the canary is exposed continuously to indicate the presence of carbon monoxide and that it works automatically, whereas with the iodine pentoxide indicator frequent determinations are necessary to indicate the presence of carbon monoxide. Furthermore, persons with poor eyesight or color blindness may be unable to read the scale and make the necessary color comparisons; persons so affected should not be intrusted with this device. On the other hand canaries and Japanese waltzing mice have the disadvantages previously detailed.

Acetylene, alcohol, ammonia, benzine, ether, ethylene, gasoline, hydrogen sulfide, hydrogen chloride, and natural gas containing some higher hydrocarbons color the Hoolamite when no absorbent such as activated charcoal is interposed between the Hoolamite tube and the source of the gas to be tested, but with activated charcoal placed in the barrel of the detector no color is visible. Carbon dioxide, carbon tetrachloride, chlorine, hydrogen, methane, nitrogen peroxide, phosgene, and sulfur dioxide have no effect on the Hoolamite tubes.

5. Determination

The sampling methods detailed in Chapter II are, in general, suitable for sampling atmospheres for the estimation of carbon monoxide. Particular attention is called to the continuous sampling device of Goldman and Mathis[38a] described in Chapter II for this purpose.

a. Iodine Pentoxide Method [39-43]

This method depends on the same reaction as the method described in the previous section. It is generally used as a reference method, for it is accurate for all concentrations of carbon monoxide. It is necessary, however, to take special precautions for concentrations above 0.3 per cent.[43a]

The gas sample is first passed through a U-tube containing small pieces of potash, then over pumice impregnated with sulfuric acid, and finally through a U-tube containing iodine pentoxide immersed in an oil bath at 150° C. An absorption tube containing 10 ml. of sodium hydroxide solution is used for absorbing the carbon dioxide formed and the iodine liberated.

The iodine pentoxide tubes may be made of $^3/_4$-inch Pyrex tubing with a U about 10 inches long. They may be filled with alternate layers of glass wool and iodine pentoxide, each tube containing 30 to 40 g. of the latter. The arm on the exit side of the U-tube should be somewhat longer than the other, and tapered to make an interlocking glass joint with the guard tube. A similar glass ground connection should be made with the absorption bulbs on the entrance side to eliminate the errors due to rubber connections.

The preparation of iodine pentoxide is important. If the iodine pentoxide is not dry, iodine is produced even when carbon monoxide is absent.

[38a] D. E. Goldman and J. A. Mathis, *Naval Med. Research Inst., Research Project* X-417, *Rept. 4* (1945).

[39] A. Gautier, *Compt. rend., 126,* 793, 931 (1898).

[40] M. Nicloux, *Compt. rend., 126,* 746 (1898); *154,* 1166 (1912).

[41] L. P. Kinnicutt and G. R. Sanford, *J. Am. Chem. Soc., 22,* 14 (1900).

[42] L. R. Pire, *Anales soc. españ. fis. quim., 27,* 192 (1929).

[43] G. Lunge and C. A. Keane, *Technical Methods of Chemical Analysis,* Van Nostrand, New York, 1924.

[43a] F. H. Goldman, A. A. Coleman, H. B. Elkins, H. H. Schrenk, and C. A. Smucker, *Am. Pub. Health Assoc. Yearbook, 1940–41,* 118.

In order to dehydrate iodic acid to iodine pentoxide it must be heated at 196° C. or above. It is preferably prepared from iodic acid made by the oxidation of iodine with chloric acid by heating for about 15 hours.

Teague[44] modified this method somewhat. The iodine pentoxide should be conditioned after the assembly of the apparatus by raising the temperature to 220 to 230° C. for several hours while air is being drawn through the apparatus. The purifying train may be eliminated by passing the gas sample through a tube immersed in liquid air. At this temperature, all the water, carbon dioxide, gasoline vapor, and other saturated and unsaturated hydrocarbons are removed by condensation. The sample is drawn from the gas collector through the U-tube in the liquid air, through the iodine pentoxide in a U-tube at 150° C., and through a small trap, and the liberated iodine is caught and absorbed in an absorber containing a 10 per cent potassium iodide solution. This is titrated with 0.002387 N sodium thiosulfate solution, 1 ml. of which is equivalent to

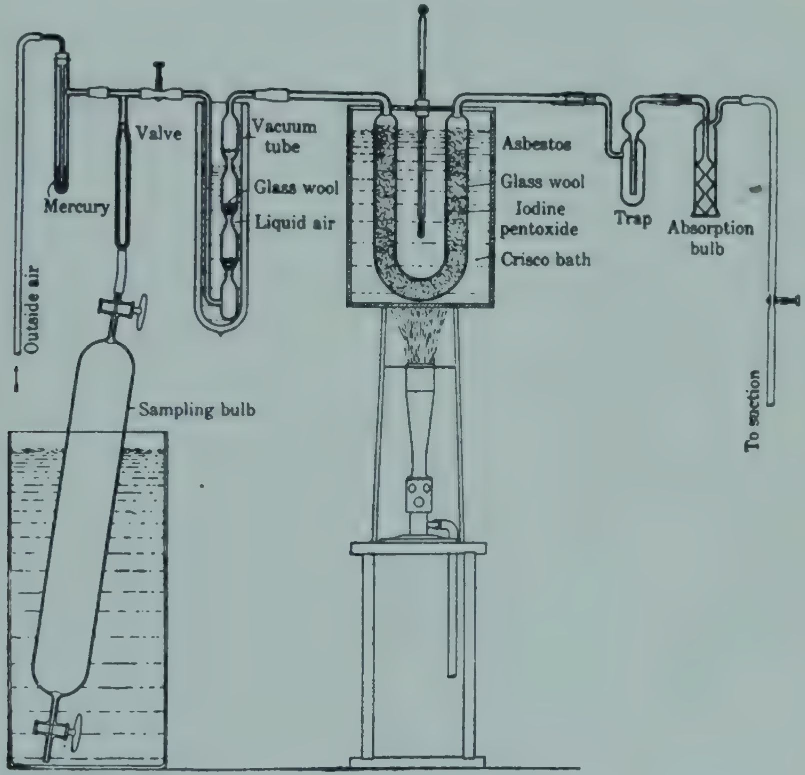
Valve
Vacuum tube
Glass wool
Liquid air
Mercury
Outside air
Sampling bulb
Asbestos
Glass wool
Iodine pentoxide
Crisco bath
Trap
Absorption bulb
To suction

Fig. 95. Diagram of iodine pentoxide apparatus.[44]

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[44] M. C. Teague, *Ind. Eng. Chem.*, *12,* 964 (1920); *U. S. Bur. Mines, Monograph 1,* 51 (1927).

0.15 ml. of carbon monoxide at 25° C. and 760 mm. pressure, or 1.5 parts of carbon monoxide in 10,000 parts of air for a 1-liter sample. A 1-liter sample is drawn through the apparatus in about 15 minutes and then is displaced by outside air at the same rate of flow.

This method is particularly adapted for the examination of the carbon monoxide content of automobile and other gas-engine exhaust gases. The iodine liberated may also be estimated spectrophotometrically.[44a]

b. Hopcalite Method [45,46]

Hopcalite is a general name for catalysts of a certain group that are capable of converting carbon monoxide to carbon dioxide at ordinary temperatures while leaving hydrogen unaffected. Hopcalite I was the name used to designate the mixture:

Manganese dioxide, MnO_2	50%
Cupric oxide, CuO	30%
Cobaltic oxide, Co_2O_3	15%
Silver oxide, Ag_2O	5%

The physical characteristics of the catalyst have a great deal to do with its efficiency.

A cheaper and very likely more widely used type of Hopcalite catalyst is composed of manganese dioxide, 60 per cent, and cupric oxide, 40 per cent, (8- to 14-mesh granules).[47]

This catalyst is used in two ways as may be noted from the equation:

$$2CO + O_2 \longrightarrow 2CO_2 + \text{(67,960 gram-calories per gram-molecule of CO)}$$

That is, either the heat produced in the reaction may be measured by some electrical device or the carbon dioxide produced may be estimated by one of the methods detailed in a subsequent section.

Automatic Devices. A number of continuous carbon monoxide recorders for small concentrations in air have been described.[48-51] In some devices the oxidation of the carbon monoxide as it comes in contact with the granular Hopcalite catalyst results in a temperature rise in the air stream within the catalyst cell, which is transmitted to a recording potentiometer through a series of differential thermocouples. The cell potential is directly proportional to the carbon monoxide concentration in the absence of readily oxidizable or inhibiting impurities that affect the catalyst.

[44a] B. Smaller and J. F. Hall, Jr., *Ind. Eng. Chem., Anal. Ed., 16,* 64 (1944).

[45] A. B. Lamb, W. C. Bray, and J. C. W. Fraser, *Ind. Eng. Chem., 12,* 213 (1920).

[46] J. C. W. Fraser and C. C. Scalione, U. S. Patent 1345323 (1920).

[47] A. B. Lamb, C. C. Scalione, and G. Edgar, *J. Am. Chem. Soc., 44,* 738 (1922).

[48] A. C. Fieldner, S. H. Katz, and E. G. Meiter, *Eng. News-Record, 95,* 423 (1925).

[49] S. H. Katz, D. A. Reynolds, H. W. Frevert, and J. J. Bloomfield, *U. S. Bur. Mines, Tech. Paper 355* (1926).

[50] S. H. Katz and H. W. Frevert, *Ind. Eng. Chem., 20,* 564 (1928).

[51] H. W. Frevert and E. H. Francis, *Ind. Eng. Chem. Anal. Ed., 6,* 226, (1934).

To remove moisture and other condensable components the air sample is passed through a train of concentrated sulfuric acid, soda lime and charcoal, and calcium chloride, before passing through the Hopcalite catalyst. In practice the use of sulfuric acid as an air drier is objectionable because of its corrosive nature and the difficulties of frequent renewal and disposal. Frevert and Francis[51] developed a modified form of analyzer, in which the acid train, whose chief function is the removal of moisture, is replaced by duplicate adsorbers using either silica gel or activated alumina. Alumina of 1.2 to 2.4 mm. size is probably adequate.

One variation of this method is the portable M. S. A. carbon monoxide indicator. This device[51a] comes in several models. In one of these a small pump draws the sample continuously into the instrument. The sample first passes through a flowmeter, consisting of an orifice and a differential pressure gauge. The latter is used to maintain a constant flow by having a constant differential on the flowmeter through adjustment of a volume control valve. The sample passes through a dehydrating canister, which removes any moisture, and from the canister it enters the cell containing the Hopcalite, after which it passes out of the exhaust valve of the pump. In the Hopcalite cell any carbon monoxide present in the air stream is oxidized to carbon dioxide. The heat liberated by this reaction is directly proportional to the amount of carbon monoxide present and is measured by a series of thermocouples in series with the indicating meter. The meter is calibrated to read directly in percentage of carbon monoxide and has a scale range from 0 to 0.15 per cent carbon monoxide graduated in hundredths of a per cent. It can be read directly to 0.005 per cent and estimated to 0.01 per cent, or 10 parts per million. The sensitivity of this carbon monoxide indicator is reduced when operated in temperatures below freezing.

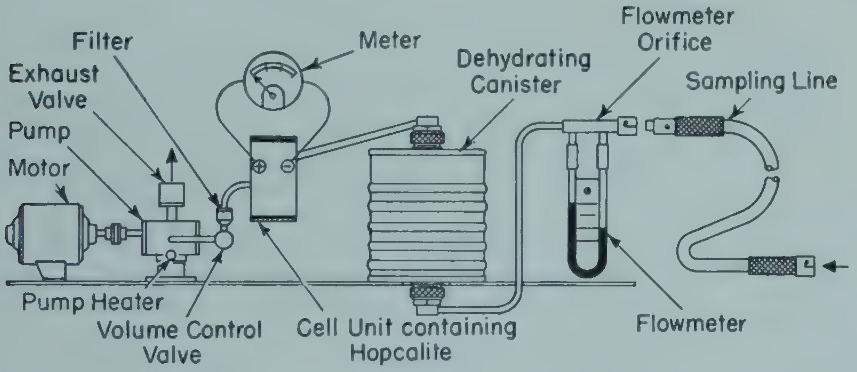

Fig. 96. Hopcalite carbon monoxide indicator.

[51a] Mine Safety Appliances Co., Pittsburgh, Pa.

The small amount of Hopcalite in the cell should be renewed after 8 hours of actual service. The canister for removing moisture should be replaced after 20 hours of service.

In another model, a hand-operated pump, analogous to that described for the midget impinger, is used to draw the air sample through the Hopcalite.

Such indicators must be set to zero by passing carbon monoxide-free air through them. The motor-driven device requires 15–30 minutes for adjustment, while the hand-driven model is equilibrated for 2 minutes before adjusting the meter needle. To overcome this difficulty and the errors involved attributable to deflections caused by change in temperature when the instrument is moved or because of needle drift, Setterlind[51b] mounted an additional canister of the universal type plus a three-way stopcock on the device. The additional canister removes carbon monoxide by means of the Hopcalite it contains, providing a carbon monoxide-free air stream.

The air inlet is connected to the common branch of the stopcock, and the top of the canister to one of the others by means of tubing.

In use the instrument is taken directly to the point of testing, the flap on the bottom of the universal canister is opened, the valve is turned to let the air pass through the canister, the motor is started, and the air flow is adjusted. After the device has warmed up, the needle is adjusted to zero and the amount of drifting observed. If the drift does not exceed 1 division in 3 minutes, the instrument is ready to use. The needle is then adjusted accurately to zero and the stopcock is turned to a position letting the air directly into the indicator. If carbon monoxide is present, the indicator will start registering within 10–30 seconds, depending upon whether or not an extension hose is being employed. A maximum should be reached in about 1 minute and the reading recorded. The valve may now be moved to the purge position, the indicator taken to the next test position, and the operation repeated.

If the response to carbon monoxide is sluggish, after the instrument has been serviced, the lag is probably attributable to dirt accumulating in the orifice of the flowmeter. Periodic cleaning of the orifice and the three-way stopcock is essential.

c. Palladious Chloride Method

By means of the following method the amount of carbon monoxide in air can be ascertained quantitatively from the reduced palladious chloride.[52] A definite volume of palladious chloride solution is exposed to the air containing carbon monoxide and after the reaction is complete, the excess chloride is separated from the metallic palladium by filtration and this excess palladious chloride is estimated colorimetrically. The reactions that occur are probably the following:[53]

[51b] A. N. Setterlind, *Ind. Hyg. Newsletter, 7*, No. 4, 8 (1947).

$$PdCl_2 + CO \longrightarrow Pd + COCl_2$$
$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

The addition of potassium iodide, in excess of that required to precipitate the palladious chloride as palladious iodide, dissolves the latter salt to yield a red solution, which, in the presence of a protective colloid such as gum ghatti or gum arabic, remains perfectly clear for at least 24 hours.

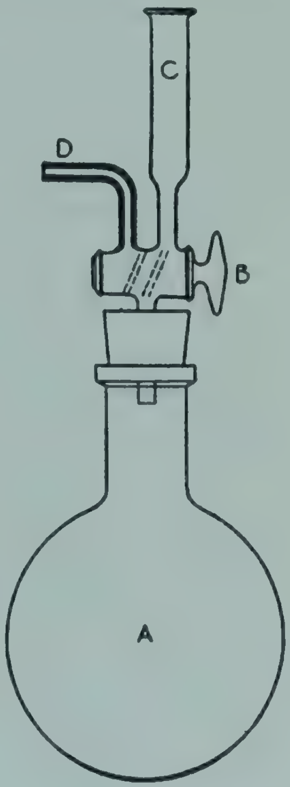

Fig. 97. Apparatus for the determination of carbon monoxide by palladious chloride.

Reagents. Gum Ghatti Solution.—Add 5 g. of gum ghatti to 500 ml. of water and allow to stand for 24 to 48 hours with occasional shaking. After filtration, a clear solution results. It becomes slightly turbid on standing and must be refiltered from time to time.

Palladious Chloride Solution.—Dry 500 mg. of palladious chloride at 100°C. for 1 hour. Place the dried salt in a beaker and cover with 150 ml. of water, add 2.5 ml. of concentrated hydrochloric acid, and heat the mixture until complete solution of the palladium chloride results. After cooling, transfer this solution to a 500-ml. volumetric flask and make up to volume. Analyze the resulting solution by the standard gravimetric method, which consists of the precipitation of palladium in acid solution as the salt of dimethylglyoxime,[54,55] to obtain the palladious chloride content. If large volumes of this solution are made it is advisable to store it in a number of well-stoppered, small bottles rather than in one large bottle, to minimize the deterioration due to exposure to air and dust when aliquots are removed for use.

Apparatus. The apparatus (Fig. 97) required for this determination consists of a 500-ml. round-bottomed, short-necked Pyrex flask, fitted through a one-hole rubber stopper with a two-way stopcock. The volume of the flask with the stopcock in position must be determined, and for convenience in calculation it is desirable that any flasks used be of approximately the same volume, around 500 ml. One of the upper outlets of the stopcock is fitted with a small reservoir, which has a capacity of approximately 7 ml. The second upper outlet of the stopcock is a tube extending upward for 2 to 3 cm. and is then bent at right angles away from the reservoir for another 2 to 3 cm. The lower outlet of the stopcock is cut off at approximately 4.5 cm. and protrudes through the lower surface of the stopper far enough, about 0.5 to 1.0 cm., to ensure the passage of the palladium chloride solution into the flask without contact with the stopper. The inside diameter of the tube should be less than 1.5 mm.

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[52] A. A. Christman, W. D. Block, and J. Schultz, *Ind. Eng. Chem., Anal. Ed., 9,* 153 (1937).

[53] L. W. Winkler, *Z. anal. Chem., 97,* 18 (1934).

[54] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis,* Wiley, 1929.

[55] H. C. Diehl, *Applications of the Dioximes to Analytical Chemistry,* Iowa State College, Ames, 1940.

Attach the flask to a vacuum pump, connected with a manometer, evacuate to less than 1 mm. of pressure, and close the stopcock. There should be no appreciable change in the pressure within the flask at the end of 24 hours, provided the stopcock is properly ground and greased and all rubber connections are tightly fitted. Stopcocks that do not meet these requirements should not be used. Lubricants which contain ingredients that react with palladium chloride must not be used.[58] Flasks prepared as described may be used to obtain the samples by opening the stopcocks of evacuated flasks and then closing the stopcocks again after equilibrium has been established. Other vacuum sampling devices of known volume may also be used.

Procedure. Connect the side tube of a flask containing the sample to be analyzed to the side tube of another evacuated flask of approximately equal volume by means of pressure tubing. Turn the stopcocks of both flasks so that the contents of the flasks are brought into equilibrium. Place 3 ml. of the palladious chloride solution and 0.2 ml. of 10 per cent aluminum sulfate solution into the reservoir and transfer quantitatively to the flask by means of three 1-ml. washings of water. Take care at all times to prevent the access of air to the flask. Shake the flask at intervals for the next 2 hours, particularly during the period when the major part of the metallic palladium is forming, to prevent the formation of a layer of metallic palladium on the surface of the liquid which will prevent the free access of the carbon monoxide to the palladium chloride. The presence of aluminum sulfate facilitates the flocculation of the colloidal palladium. After the period of shaking, allow the flask to stand overnight, or for at least 4 hours.

Separate the excess of palladium chloride quantitatively from the metallic palladium by filtration through quantitative filter paper into a 50-ml. volumetric flask. The volume of liquid in the 50-ml. flask, after the apparatus and the filter paper have been thoroughly washed, should be 25–30 ml. The filtrate should be prefectly clear. Add 2 ml. of gum ghatti solution and mix. Add 5 ml. of freshly prepared 15 per cent potassium iodide solution and swirl. Since it has been found that small amounts of palladium chloride are adsorbed by the filter paper, remove these last traces by washing the filter twice with 2-ml. portions of 15 per cent potassium iodide solution, and once with a 1-ml. portion. Each washing with potassium iodide solution is followed by small volumes of water. Filter these washings directly into the colored solution already in the volumetric flask and make to volume with water. Add a trace of caprylic alcohol to the flask to minimize the foaming attributable to the gum ghatti solution.

Prepare the standard for the colorimetric comparison by the addition of 2 ml of the palladious chloride solution, 25 ml. of water, 2 ml. of gum ghatti solution, and 10 ml. of 15 per cent freshly prepared potassium iodide solution to a 50-ml. volumetric flask. Add the potassium iodide solution while swirling and make up to volume. The color produced by the addition of potassium iodide reaches maximum intensity in a few minutes and remains constant for at least 24 hours. The standard color is set at 20 mm. when matched in a colorimeter.

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[58] Lubriseal (Arthur H. Thomas Co.) is satisfactory.

Sample Calculation. Assume the volume of the sampling flask and the flask with which it is to be equilibrated is 530 ml. The sample of air is taken at 23° C. and 744 mm. pressure. From the colorimetric determination of the excess palladious chloride it is calculated that 1.582 mg. of palladious chloride had been reduced by carbon monoxide. This reduction is due to the carbon monoxide in 265 ml. of air, since the flasks, to which the palladious chloride solution was added, were at a pressure of half that at which the sample was taken, approximately 0.5 atmosphere. One milligram of palladious chloride is reduced by 0.1261 ml. of carbon monoxide at 0° C. and 760 mm. pressure. Therefore:

$$1.582 \times 0.1261 \times \frac{760}{744} \times \frac{296}{273} + \frac{10{,}000}{265} = \text{8.34 parts of carbon monoxide per 10,000 parts of air}$$

In general, the factors $\frac{0.1261 \times 760 \times 10{,}000}{273}$ will appear in all calculations. They are equivalent to the factor 3,510.4. Hence the simplified equation for all calculations is

$$3{,}510.4 \times \frac{T}{PV} \times \text{mg. PdCl}_2\text{ reduced} = \text{parts of CO per 10,000 parts air}$$

where:

T = absolute temperature at which sample was taken
P = barometric pressure in mm. at which sample was taken
V = volume of air taken for analysis. In above example, 265 ml.

Because there is a loss of palladious chloride, which is greater in the presence of larger amounts of metallic palladium, Christman[56a] and coworkers recommend the following corrections in order to avoid high results for carbon monoxide.

$PdCl_2$ reduced, mg.	Subtract from calculated CO values
0.5	0.19
1.0	0.28
1.5	0.33
2.0	0.38

If the air under examination contains unsaturated hydrocarbons or hydrogen sulfide in amounts which would yield high results for carbon monoxide, these interfering substances may be effectively removed by successive passage of the gas through a scrubber solution of bromine water and a 33 per cent potassium hydroxide solution. The bromine solution is prepared by adding one volume of water to two volumes of saturated bromine water. To every 100 ml. of this mixture, add 5 g.

[56a] A. A. Christman, W. D. Block, and J. Schultz, *Ind. Eng. Chem., Anal. Ed.*, *9*, 153 (1937).

of potassium bromide. Sintered-glass aeration tubes are to be preferred to insure efficient washing.

Prior to taking a sample for analysis, the gas under examination must be forced through the scrubber solutions until the gas above these solutions has been replaced. The gas is then drawn through the scrubber solutions into the analysis flask at a slow rate to ensure complete absorption of the interfering substances. The rate of passage must be slow to permit the complete removal of bromine vapor by the alkali. After the air has stopped bubbling through the absorbent solutions, an aspirator bulb is attached and air is forced through the solutions and into the analysis flask until a slight positive pressure within the flask is obtained. The flask is then disconnected from the scrubber system and the stopcock opened momentarily to allow the flask to come to atmospheric pressure.

Where a pump is not available that will evacuate the flasks to 1 mm. pressure, sampling may be performed by the vacuum-bottle method, as described in Chapter II. If interferences are not present, sampling by liquid displacement may also be made.

This quantitative method is useful as a laboratory method but cannot be used to detect carbon monoxide in the field.

d. Phosphomolybdate Method[57]

In this method a measured volume of air sample is brought into contact with an acid solution containing palladium chloride, phosphomolybdic acid, and acetone. The sample is equilibrated with the solution by rotation in a bath at 60°C., during which operation reactions take place that result eventually in the production of molybdenum blue by reduction of the phosphomolybdic acid. The intensity of the molybdenum blue produced is proportional to the concentration of carbon monoxide in the air sample and may be expressed in terms of carbon monoxide by a colorimetric comparison with standards representing known concentrations of carbon monoxide. The color comparisons may be made conveniently with a photoelectric colorimeter.

The method is sensitive to approximately 0.001 per cent by volume of carbon monoxide and the range is 0 to 0.06 per cent. The accuracy of the method decreases with increasing concentration of carbon monoxide; at 0.06 per cent the accuracy is about ±0.005 per cent of carbon monoxide. Concentrations somewhat higher than 0.06 per cent may also be determined but with decrease of accuracy. The range may be extended without significant sacrifice in accuracy by dilution of the original air sample with known proportions of carbon monoxide-free air.

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[57] R. D. Polis, L. B. Berger, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest.*, 3785 (1944).

As the method is based upon a reduction reaction, it is not specific for carbon monoxide and other gases that exert a reducing effect will interfere with the determination of carbon monoxide. Therefore the method is applied most satisfactorily to samples known not to contain interfering gases, or to samples from which interfering gases may be removed before the determination of carbon monoxide. The effects on the method of gases other than carbon monoxide are discussed below.

Reagents. Palladium Chloride Solution.—Weigh 0.5 g. of the chemically pure palladious chloride in a beaker. Add 2 ml. of concentrated hydrochloric acid and approximately 100 ml. of water. Cover the beaker with a watch glass and heat until the salt is dissolved. Transfer the solution to a 250-ml. volumetric flask, add 3.5 of concentrated hydrochloric acid, and, after cooling, dilute with water to the indicated flask volume.

Phosphomolybdic Acid Solution.—Dissolve 5 g. chemically pure phosphomolybdic acid, $20MoO_3.2H_3PO_4.48H_2O$, in water and dilute to 100 ml.

Acetone.—Use reagent-grade acetone. Considerable variation may be observed in the suitability of different lots of acetone obtained from different manufacturers, although lots may meet the specifications of the American Chemical Society for reagent-grade material. Some lots of acetone are suitable for use as received, while others may cause color production in the reagent without contact with carbon monoxide. Unsuitable acetones can be made fit for use in this method by refluxing for 1 hour with potassium permanganate or by contact with permanganate at room temperature for 48 hours. After this treatment the acetone is dried over anhydrous potassium carbonate and distilled.

Mixed Carbon Monoxide Reagent.—Mix equal volumes of the solutions of palladium chloride, phosphomolybdic acid, and 3 N sulfuric acid. Age the mixed reagent for 48 hours at room temperature before use or hasten the aging process by maintaining the reagent at 60° C. for 4 hours. The reagent tends to darken on standing at room tem-

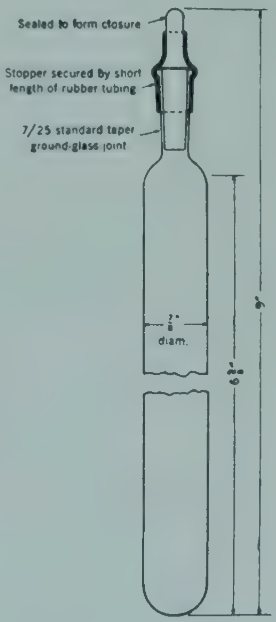
Sealed to form closure
Stopper secured by short length of rubber tubing
7/25 standard taper ground-glass joint
diam.

Fig. 98. Test tube in which reactions are carried on and comparisons of color are made.[57]

perature, but this does not interfere with the final results as long as the colorimeter may be adjusted with a reagent blank to compensate for the darkening of the reagent. Change in color may be prevented by storing the reagent in a refrigerator.

Collection of Sample. Collect the air samples in or transfer them to special 50-ml. glass-stoppered tubes (Fig. 98). These are optically matched test tubes modified by sealing to them ₮ 7/25 ground-glass joints, the male portion of which is sealed to form a closure. The volume of the tube is approximately 50 ml. Calibrate each tube and etch its volume on the upper portion of the tube. By using optically matched tubes the reaction between sample and reagents and the color comparison may be carried out in the same tube. Introduce the sample into the tube by water displacement. It has been found advisable to fill the tubes with distilled water when not in use and to use only distilled water in washing the tubes. Care must be exercised also to prevent introduction of droplets of mercury or other extraneous material into the tubes. When it is desired to transfer the sample from some other type of container the apparatus shown in Fig. 99 may be used. When the carbon monoxide content of the sample is expected to exceed the maximum of the normal

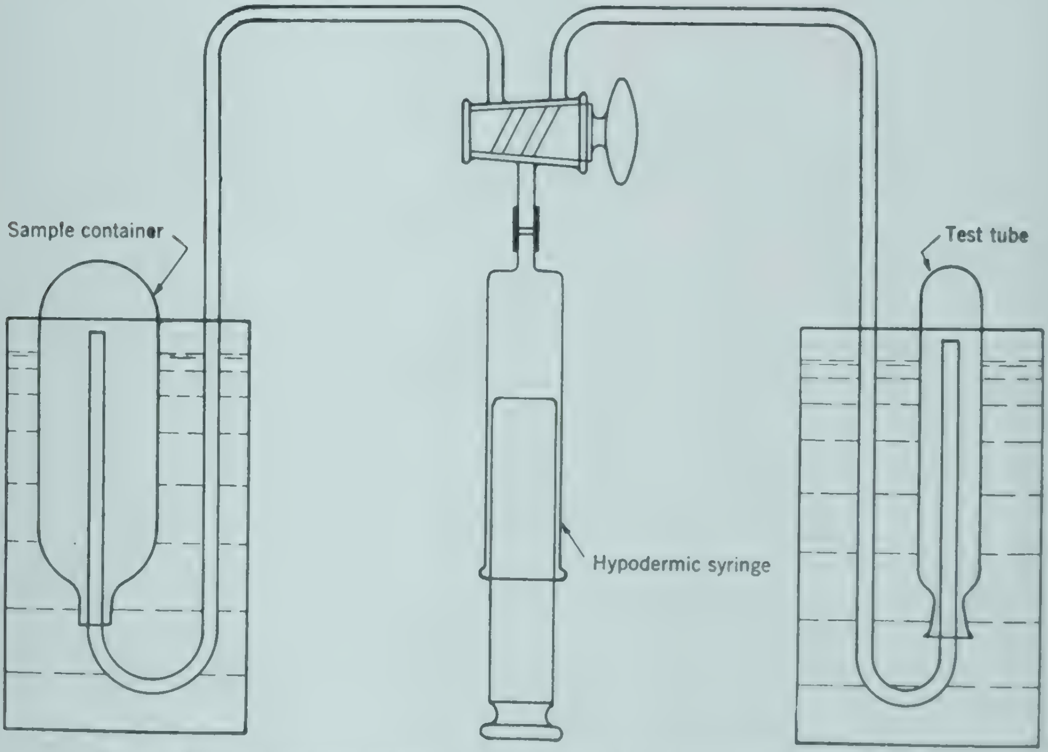

Fig. 99. Diagrammatic sketch of apparatus for transferring air sample from sample container to test tube.[57]

range of the method (0.06 per cent), dilute the sample by introducing a measured volume into the tube by the use of a hypodermic syringe fitted with a U-shaped needle and then displace the remaining water in the tube with carbon monoxide-free air. Drain excess water from the interior surfaces of the tube by removing the stopper momentarily and inverting the tube upon a towel.

Procedure. Add 3 ml. of the carbon monoxide reagent, then 3 ml. of the acetone reagent, and insert the stopper. Carry out this step rapidly to minimize the possibility of dilution of the tube contents with air. Fasten the stopper in place with a short length of rubber tubing (Fig. 98). When a number of samples are to be analyzed, it has been found convenient to add the carbon monoxide reagent to all the tubes first, and then the acetone.

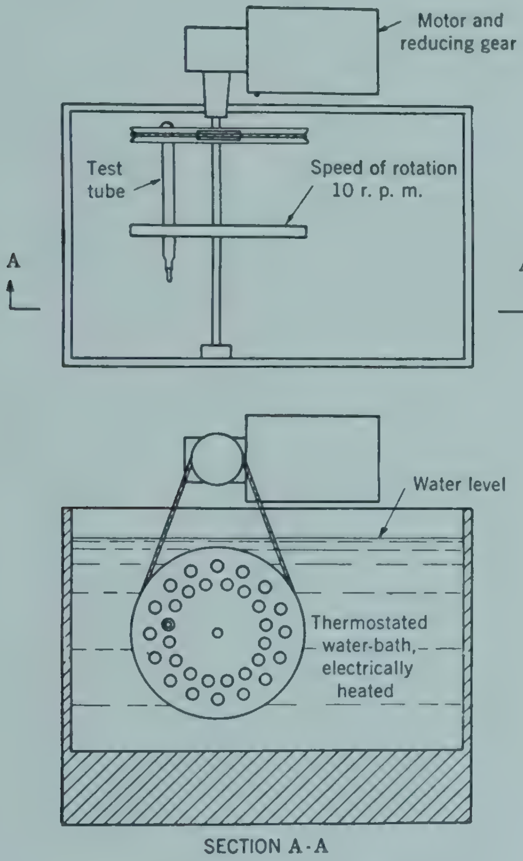
Motor and reducing gear
Test tube
Speed of rotation 10 r. p. m.
A
A
Water level
Thermostated water-bath, electrically heated
SECTION A-A

Fig. 100. Diagrammatic sketch of apparatus for equilibrating air sample and reagent at constant temperatures.[57]

With each sample or group of samples analyzed a blank determination is made with carbon monoxide-free air. Note that the air must be carbon monoxide-free; trace amounts of carbon monoxide from laboratory burners or other sources may affect the results. The analysis of a blank sample is important in obtaining satisfactory results and should always be made with the same lot of reagents that has been used with the samples under analysis.

Equilibrate the samples and the blank by rotation for 60 minutes in a water bath at 60° C. with the aid of a device similar to that shown in Fig. 100. The water-bath temperature should be controlled to ±1° C. The time of equilibration should be exact also, as color intensity increases at a lesser rate on further heating. The color developed in 60 minutes at 60° C. was found to remain essentially constant for 24 hours after the tubes are cooled to room temperature.

Clean the exterior of each tube after equilibration by immersion to the neck in chromic acid cleaning solution. Wash, dry, and cool the tubes.

Color Comparison. Measure the color intensity of the molybdenum blue, using a filter having a transmission band of 635 to 720 millimicrons. In making color comparisons, insert the tube containing the blank determination with carbon monoxide-free air in the instrument and adjust the galvanometer to read 100 per cent transmission. If the galvanometer scale consists of 100 equal divisions, the galvanometer readings obtained with samples or standards containing carbon monoxide may be taken directly as percentage transmission compared with the blank.

e. Pyrotannic Acid Method

The pyrotannic acid method is adapted to rapid and accurate determination of small amounts of carbon monoxide in air. It will not indicate more than 0.2 per cent. Therefore, if more than this amount is present, other means of estimation should be employed for quantitative results, such as the NBS indicator, the MSA indicator, the Hoolamite detector, iodine pentoxide method, and volumetric methods. In the range of low percentages, from 0.01 per cent to approximately 0.2 per cent, the pyrotannic acid method is very accurate, and for this reason was formerly used in preference to other methods or apparatus by the gas laboratory of the U. S. Bureau of Mines experiment station at Pittsburgh for determining or confirming the presence of low percentages of carbon monoxide in samples of mine air, especially mine-fire atmospheres. The presence of carbon monoxide, even in minute quantity, behind fire seals is always a strong indication that the fire is still burning, or at least has been burning too recently for the area to be opened with safety. It is in work such as this that the pyrotannic acid method can be used to its greatest value in the mining industry.[58]

The method[59,60] is based on the fact that a light brownish-gray suspension is formed in a few minutes when normal blood diluted with water is treated with a solution of pyrogallic and tannic acids, whereas light carmine suspensions are formed with blood having carbon monoxide in combination with hemoglobin. When compared with color standards of known concentration, the intensity of the carmine-colored suspension gives the saturation of the hemoglobin being tested. The standards used with the apparatus can be made from human or animal blood, such as guinea pig, cattle, etc. Although they are reliable for a limited time, standards prepared from blood deteriorate and are not accurate over long periods. Permanent standards may be prepared from artists' oil-color pigments, which are ready to use at all time and change color relatively little. Permanent standards are furnished with purchased equipment.

The pyrotannic acid method is adaptable for the determination of carbon monoxide in both blood and air. The procedure for the determination of carbon monoxide in air differs slightly from that for determining blood saturation. The two methods are usually called "determination of blood saturation," as in the case of a person poisoned with carbon monoxide, and "determination of percentage carbon monoxide in air," as in the investigation of contaminated atmospheres.

Apparatus. (1) A set of color standards to represent the color of blood having varying amounts of carboxyhemoglobin. The standards are contained in small, clear test tubes 5/16 inch in diameter and 2 ml. in volume. These are arranged in a suitable rack with spaces between for interposing tubes of similar size that contain the prepared blood samples for analysis.

(2) Small test tubes, 5/16 inch in diameter and 2 ml. in volume, in which to prepare specimens for analysis.

(3) A dilution pipette, which consists of a pipette with a capillary stem that holds 0.1 ml. and a bulb above that has a total volume of 2 ml., thus making a dilution of 1:20, which is the most suitable blood concentration for this test.

(4) A spring hemospast or blood lancet for making a small wound in the finger or other convenient place from which blood may be obtained.

(5) A small watch glass or spot plate for catching the blood as it flows from the wound. The blood may be drawn up directly from the bead over the wound, but the spot plate will be found convenient where two or more specimens are desired from the same wound.

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[58] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines, Miners' Circ. 33* (1938).

[59] R. R. Sayers and W. P. Yant, *U. S. Pub. Health Service, Reprint 790* (192).

[60] R. R. Sayers, W. P. Yant, and G. W. Jones, *U. S. Pub. Health Service, Reprint 872* (1924).

(6) A mixture of equal parts of pyrogallic and tannic acids, either solid or in solution. Usually it is in powdered form and is kept in a small bottle with a measuring spoon holding approximately 0.04 g., which is found to be most suitable for 2 ml. of a 1:20 blood solution. If less blood solution is used, the amount of acids used must be correspondingly decreased.

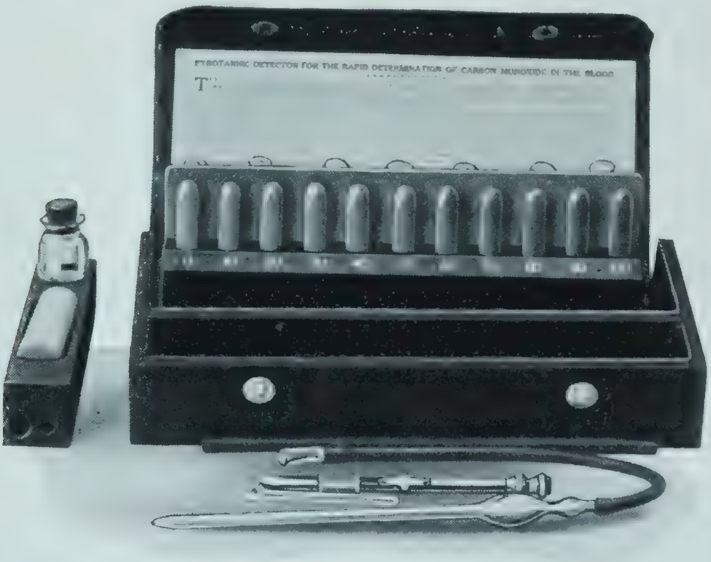
PYROTANNIC DETECTOR FOR THE RAPID DETERMINATION OF CARBON MONOXIDE IN THE BLOOD

Fig. 101. Apparatus for quantitative determination of carbon monoxide in air by the pyrotannic acid method.[60] (*Courtesy Mine Safety Appliances Co.*)

(7) Air-sample bottles of 250 ml. capacity, fitted with rubber stoppers.

(8) A rubber aspirator bulb with an attached scrubber tube containing soda lime for removing gases that might have an interfering effect.

Obtain samples of air by inserting the glass tube on the end of the soda lime scrubber into the sample bottle and aspirate the air through the sample bottle long enough to purge it of its original contents; this requires at least 25 squeezes. Expel the last bulbful of air through the sample bottle while the glass tube is being removed. Insert the rubber stopper quickly and tightly. If regular sample bottles and aspirator bulbs are not available, the samples may be collected in any ordinary bottle having a capacity of about 250 ml. by the liquid-displacement method, in which the bottle is filled with water and the bottle is then emptied at the sampling place. The walls should be well drained, as an excess of water will interfere with the accuracy of the result.

Take the collected samples to the place where the analysis is to be made, preferably away from the place where the samples were obtained.

The blood to be used in making the analysis may be taken from a stock solution of relatively fresh human or animal blood or from a person who has not been exposed to carbon monoxide. Make a small puncture wound, approximately 2 mm. deep, with the hemospast in the tip of the finger of the person whose blood is to be used. Catch several drops of blood on the spot plate or draw the blood directly into the pipette. If the blood does not flow freely, wrap the finger with rubber hose, beginning at the base and progressing toward the tip; massaging the finger also aids the flow. When the blood has been produced, draw it quickly into the stem of the pipette to the 0.1-ml. mark. Hold the pipette horizontal and remove any blood on the exterior of the tip. Raise the tip slightly and permit a little of the blood to flow into the diluting bulb. Insert the pipette quickly into a bottle of water and by using suction at the same time fill to the 2-ml. mark to give the proper dilution.

Transfer the 2 ml. of blood solution to the sample bottle, being careful to allow as little air to escape from the bottle as possible. It is best first to discharge the solution from the pipette into one of the small test tubes and to pour from this tube into the sample bottle. After the blood solution has been added to the bottle, replace the stopper tightly, hold the bottle horizontal, and rotate constantly for 15 to 20 minutes, avoiding violent shaking and agitation. After the 15 to 20 minutes, when equilibrating has been finished, pour the blood solution back into the same test tube used for the transfer, add approximately 0.04 g. of the pyrogallic-tannic acid mixture, and invert the tube gently several times to insure thorough mixing with the reagents.

Place the tube in a rack and allow to stand 15 minutes at room temperature. If particles of the solid acids settle out, invert the tube several times more. At the end of the 15-minute period compare the sample with the standards by interposing it between them until the standard is found which most nearly matches the unknown. If carbon monoxide is indicated the sample should be allowed to stand 15 minutes longer and another reading made. The latter reading should be taken as the more accurate.

The equilibrating should be done in a rather dimly lighted place. When the sample bottle is rotated, as much of the surface of the bottle as possible should be covered with blood solution. Every now and then the solution should be thrown centrifugally from the sides to the bottom of the bottle by a quick swirling motion, which allows a new surface to form and aids in reaching equilibrium of the gases in the air above the blood and the blood solution. When a large number of samples have to be analyzed a motor-driven equilibrator will save time. On this machine or similar types, sample bottles are held at a 60-degree angle from a revolving vertical disk, the speed of revolution being such as to allow the solution to flow over the inner surface of the bottles.

To transpose the amount of blood saturation obtained in the sample bottle to the percentage of carbon monoxide in the air, several formulas are used, as described by Sayers and his co-workers. To simplify the operation of making computations and applying all the corrections for the calculation of the carbon monoxide content in the air, the graphs of Fig. 102 may be used. These graphically represent the calculations and corrections from which the carbon monoxide content in air can be determined from the blood saturation. The original papers of Forbes and Grove should be consulted.

The pyrotannic acid method is a quick, efficient, and accurate means for ascertaining the amount of carbon monoxide in air. It will indicate low percentages of carbon monoxide. Its deficiency lies in the inability to calculate the amount of carbon monoxide directly and the difficulty, at times, of obtaining normal blood.

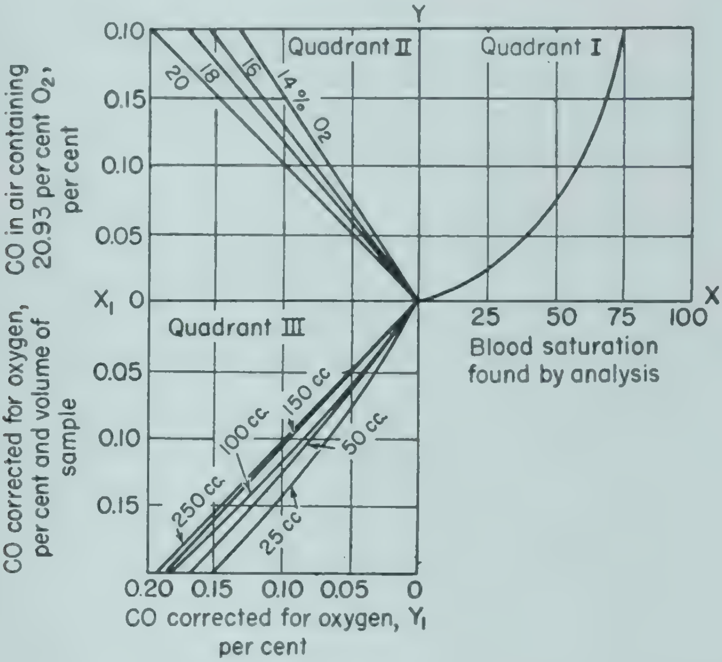

Fig. 102. Curves for calculating per cent carbon monoxide.[58]

B. CARBON DIOXIDE

1. Increasing Industrial Use and Dangers

Carbon dioxide is able to paralyze the respiratory center. Because of this action it is an industrial hazard. It is heavier than air (sp. gr., 1.529) and thus may collect in manholes, mine floors, ship holds, wells, brewery vats and similar vats, garbage dumps, etc. Furthermore, because of its heaviness, it does not tend to diffuse away readily. It is the product of complete combustion of carbonaceous material and so occurs where fires are present or where explosions have occurred. Where persons are working in a confined space, the amount of carbon dioxide formed by the breathing of these workers may assume dangerous proportions.

The dangers associated with carbon dioxide are increasing with increasing use of this substance. It is now used extensively in a solid form, known as "Dry Ice," as a refrigerant. In the liquid state it is employed for charging water and in a special Bureau of Mines permissive cartridge for the blasting of coal.[61]

In 1936 in Brooklyn, several persons were asphyxiated while working in the hold of a ship in which solid carbon dioxide was the refrigerant.[62] This instance shows that wherever solid carbon dioxide is used in poorly ventilated quarters it is a serious hazard. There have been serious airplane accidents because of its use as a fire extinguisher.

Blackdamp is the term applied to atmospheres depleted of oxygen containing relatively large proportions of carbon dioxide. Haldane[63] defines blackdamp as an accumulation of carbon dioxide and nitrogen in proportions larger than that found in pure air. This term is often used in miners' terminology.

2. *Physiological Response*

Carbon dioxide is a noncombustible, colorless, odorless, slightly acid gas. It is the regulator of the breathing function. An increase in the amounts of carbon dioxide breathed results in an increased rate of breathing. High concentrations, however, paralyze the respiratory center, resulting in asphyxiation and death. Its concentration in some atmospheres is sufficient to cause symptoms in man, or even unconsciousness and death.[64–66] One-half of 1 per cent by volume of carbon dioxide in normal air causes a slight and unnoticeable increase in the ventilation of the lungs; that is, a man exposed to 0.5 per cent of carbon dioxide will breathe a little deeper and a little faster than when in pure air. If there is 2 per cent of carbon dioxide in the air the lung ventilation will be increased about 50 per cent; if there is 3 per cent the lung ventilation will be increased about 100 per cent; 5 per cent causes about 300 per cent increase in the lung ventilation and breathing is laborious; 10 per cent can be endured for only a few minutes. With 12 to 15 per cent the person soon becomes unconscious, and death may take place after exposure for several hours to 25 per cent. The generally recommended maximum allowable concentration is 5,000 parts per million.

[61] J. E. Tiffany, *U. S. Bur. Mines, Rept. Invest. 2920* (1929).

[62] J. A. Gonzales, M. Vance, and M. Helpern, *Legal Medicine and Toxicology*, Appleton-Century, New York, 1937.

[63] J. S. Haldane, *Trans. Inst. Mining Engrs. (London), 8,* 567 (1894–95).

[64] *Fed. Bd. Vocational Education, Coal-Mine Gases, Bull. 39* (1931).

[65] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines, Miners' Circ. 33* (1937).

[66] R. R. Sayers, *U. S. Bur. Mines, Tech. Paper 334* (1923).

3. *Classification of Methods for Determination of Carbon Dioxide*

The volume and amount of carbon dioxide present in an atmosphere may be ascertained by a number of methods. These have been classified by Martin and Green[67] as follows:

(1) Gravimetric methods.

(a) Carbon dioxide absorbed in strong alkaline solutions or solid absorbents, such as soda lime and Ascarite (sodium hydroxide dispersed on asbestos fibers), and the increase in weight of absorbent determined

(b) Absorbed in dilute solution of sodium or potassium hydroxide and weighed as barium carbonate.

(c) Absorbed in a strong solution of barium hydroxide and the resulting carbonate either weighed directly or converted to the corresponding sulfate.

(2) Titrimetric methods.

(a) Carbon dioxide absorbed in a dilute standard solution of sodium or potassium hydroxide and the carbonate determined by double titration, using phenolphthalein and methyl orange or other suitable indicators.

(b) Absorbed in a standard solution of barium hydroxide and the carbonate determined by a single titration.

(c) Absorbed in a dilute standard solution of sodium or potassium hydroxide, an excess of neutral barium chloride added, and the excess of alkali titrated.

(d) Absorbed in a strong solution of barium hydroxide and the resulting carbonate filtered, washed, dissolved in a standard acid solution, and titrated.

(3) Volumetric methods.

(a) By volumetric gas apparatus. Carbon dioxide absorbed directly in strong alkali in gasometric apparatus and the decrease in the volume of the gas mixture measured at atmospheric pressure; or absorbed in strong alkali, carbon dioxide liberated in an acid solution in a gas apparatus, and its volume measured at atmospheric pressure.

(b) By manometric gas apparatus. Carbon dioxide absorbed in strong alkali and liberated in the manometric apparatus by excess acid. Volume of the gas then increased to a fixed value and its pressure measured manometrically.

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[67] W. Martin and J. R. Green, *Ind. Eng. Chem., Anal. Ed.*, *5*, 114 (1933).

(4) Electrometric methods.

(a) Electrolytic resistance method. Carbon dioxide absorbed in a standard solution of alkali, preferably barium hydroxide, and the decrease in its electrolytic conductivity measured.

(b) Thermal conductivity method. The concentration of carbon dioxide in a gas mixture is indicated by its thermal conductivity, which is determined by measuring the electrical resistance of a wire heated by a constant electric current and surrounded by the gases under study.

(5) Colorimetric method.

Carbon dioxide is absorbed in a solution of the sodium salt of phenolphthalein and its concentration is indicated by the diminution in color intensity. Trace amounts[67a] may be estimated by this method.

4. Determination

Of the various methods mentioned, the volumetric methods and the titrimetric methods for the estimation of carbon dioxide are those most frequently used.

a. Volumetric Estimation

The volume of carbon dioxide present in an atmosphere may be ascertained very simply by volumetric methods. There are numerous volumetric methods, nearly all of which depend on the principle outlined above. A sample of the gas is collected by one of the devices detailed in Chapter II. The volume of this sample is measured and then the sample is passed through an adequate portion of some absorbing agent, such as potassium hydroxide solution (300 g. of KOH in 1,000 ml. of water) or sodium hydroxide solution (200 g. of NaOH in 1,000 ml. of water), contained in a volumetric apparatus. The volume of gas remaining is now measured at atmospheric pressure and the percentage of carbon dioxide may be calculated from the contraction in volume. Among the variations of this method may be mentioned those which use the Haldane apparatus[68] and the Orsat apparatus.[69]

[67a] N. A. Spector and B. F. Dodge, *Anal. Chem., 19,* 55 (1947).

[68] L. B. Berger and H. H. Schrenk, *U. S. Bur. Mines., Inform. Circ. 7017* (1938).

[69] W. P. Yant and L. B. Berger, *U. S. Bur. Mines, Miners' Circ. 34* (1936).

b. Titrimetric Estimation with Barium Hydroxide

The carbon dioxide in an atmosphere may be estimated very simply by the following titrimetric method. Pass a known volume of the air to be examined through an efficient absorber, which can subsequently be utilized for the titration, containing a known volume of standard dilute barium hydroxide solution. A 0.10 *N* barium hydroxide solution containing barium chloride works well, for the mass-action effect of the barium chloride reduces the solubility and hydrolysis of the barium carbonate.[70] After sampling is complete connect the absorber, if possible, to a source of carbon dioxide-free air which will act as a stirring device and which will provide a carbon dioxide-free atmosphere above the liquid being titrated and so exclude the carbon dioxide of the surrounding atmosphere from interfering. Titrate the excess barium hydroxide without prior filtration with 0.0454 *N* oxalic acid, using phenolphthalein or preferably thymolphthalein as the indicator. The same strength hydrochloric acid may also be used but oxalic acid is to be preferred because this acid has little effect on the barium carbonate.[71] One ml. of 0.0454 *N* acid is equivalent to 1 mg. of carbon dioxide.[72,73]

C. CYANIDES AND NITRILES

1. Hydrocyanic Acid and Cyanides

Hydrocyanic acid, hydrogen cyanide, HCN, or, as it is often called, prussic acid, is a colorless gas with a penetrating odor resembling that of bitter almonds. It is highly toxic, acting directly on the nervous system. It can be absorbed through the skin so that masks are protective only for a short time.

Liquid hydrocyanic acid, known to the fumigation trade as liquid gas, or liquid cyanide, is a colorless fluid. It is exceedingly volatile in warm dry air, for it has a boiling point of 26° C. It is lighter than water, having a specific gravity of 0.699. Large concentrations of the gas in air provide an inflammable mixture so that care must be taken not to ignite such mixtures.

Hydrocyanic acid is used extensively as a fumigant, particularly in the fumigation of ships and of citrus trees. In the case of ships its main purpose is to rid the ship and cargo of rodents and vermin such as cockroaches. In the case of citrus trees, tent-field fumigation is practiced to control a red scale. It is finding a growing use in the fumigation field, and naturally there is an increased hazard, in destroying insect pests of plants and insect pests of man such as the louse, bedbug, flea, and mosquito, by both outdoor and building fumigation.

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[70] W. B. Mack, *Plant Physiol.*, *5*, 1 (1930).

[71] F. Sutton, *Volumetric Analysis* (11th ed.), Blakiston, Philadelphia, 1924

[72] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem.*, *11*, 523 (1919).

[73] W. Martin and J. R. Green, *Ind. Eng. Chem., Anal. Ed.*, *5*, 114 (1933).

Hydrogen cyanide is not a bactericide or germicide and therefore has no effect on the bubonic-plague bacillus or other bacteria. It protects by killing the pests that harbor the bacteria.

Apart from its principal use in the fumigation of ships, buildings, citrus trees, etc., hydrogen cyanide is used as a reagent in industry and is encountered in concentrations that may be dangerous in certain industrial processes, as for instance in blast furnaces, dyestuff works, gas works, coke ovens, tanneries, fertilizer plants, and in gold mining and gilding.

Cyanides such as potassium, sodium, and calcium cyanide find use in various industries such as the extraction of noble metals and the manufacture of organic chemicals, fertilizer, rodenticides, and explosives, and in such industrial processes as case-hardening, electroplating, metal polishing, photography, and the like.

a. Toxicity and Physiological Response

Hydrogen cyanide acts by stopping the oxidation of protoplasm in the tissue cells. With high concentrations the symptoms appear rapidly, namely, giddiness, headache, unconsciousness, and convulsions, with cessation of respiration as a result of paralysis of the respiratory center in the brain. With weaker concentrations there may be the following symptoms: Irritation of the throat, palpitation, difficulty in breathing, watering of the eyes, salivation, headache, weakness of the arms and legs, giddiness—followed by collapse and convulsions. It is not a respiratory irritant.

The following table shows the effects produced by different concentrations of hydrocyanic acid vapor.

TABLE 18

Effects of Hydrocyanic Acid Vapor[74,75]

Parts per volume (approx.)	Mg. per liter (approx.)	Effects
1 in 50,000	0.025	Slight symptoms after several hours
1 in 10,000	0.12	Very dangerous within 1 hour
1 in 500	2.5	Fatal

The generally accepted maximum allowable concentration of hydrogen cyanide is 10 parts per million. Repeated exposure to small concentrations

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[74] *Dept. Sci. Ind. Research Brit., Leaflet 2* (1938).

[75] *Analyst, 63,* 658 (1938).

of cyanides over long periods causes symptoms such as weakness, nausea, muscle cramps and paralysis of legs and arms, loss of appetite, and psychoses. The recommended maximum allowable concentration of cyanides is 5 mg. per cubic meter of air, calculated as CN.

b. Forms Used in Fumigation[76]

Hydrocyanic acid may be generated at the point or in the place to be fumigated by the reaction between sodium cyanide, sulfuric acid, and water or by the reaction between sodium cyanide, sodium chlorate, hydrochloric acid, and water, in which instance cyanogen chloride is also generated. While these extremely hazardous methods are still used, the following methods have found increasing use.

(1) Liquid hydrogen cyanide containing 20 per cent cyanogen chloride or 5 to 10 per cent of chloropicrin, trichloronitromethane, which are lachrymators and therefore act as warning agents, is spread over and into the area to be fumigated by means of spray guns or jets.

(2) Zyklon consists of an earthy substance like Fuller's earth or kieselguhr impregnated with hydrocyanic acid. This is packed in strong tin containers, which are opened in or near the place to be fumigated and the contents are spread by knocking holes in each end of the can with a special hammer and sprinkling the contents on the floor of the hold or spreading the contents in a thin layer on canvas or paper on the floor of a compartment. The hydrocyanic acid evaporates into the surrounding air. Zyklon may also be scattered by means of a pump.

(3) Another "solid type" of cyanide product is "HCN Discoids," which consist of highly porous and absorptive wood-pulp disks $3^5/_8$ inches in diameter and $^3/_{32}$ inch thick. They absorb two and a half times their weight of liquid hydrogen cyanide. They come in cans holding about 64 discoids, which contain about 1 pound of liquid hydrogen cyanide and contain in addition about 5 per cent of chloropicrin, which serves as the warning gas. The cans are opened by a special type of can opener and from the open can the discoids are shaken out on to the hold or floor. In the superstructure compartments it is necessary to scatter the discoids on paper, otherwise slight staining of floor coverings may result. The hydrocyanic acid evaporates rapidly from the discoids as in the case of Zyklon.

(4) Still another means of obtaining hydrogen cyanide is from a mixture of calcium cyanide and inert ingredients supplied in metal containers, called Cyanogas.[77] When treated with water or acids or exposed to moist air, hydrocyanic acid is liberated.

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[76] C. L. Williams, B. E. Holesendorf, and J. R. Ridlon, *U. S. Pub. Health Service, Reprint 1518* (1932).

[77] Underwriters Laboratories, Inc., *List of Inspected Appliances,* December, 1938.

c. Detection

Of the many methods for the detection and determination of hydrocyanic acid and cyanides, the pyridine-pyrazolone, the ferrocyanide test, the thiocyanate method, the benzidine-copper acetate test, the methyl orange-mercuric chloride test, the silver nitrate test, and the picric acid test will be described. Animals like rats and mice are also used. If an animal of this type remains unaffected for 10 minutes a fumigated place may be considered safe. The Prussian blue and thiocyanate reactions, which are specific for hydrogen cyanide, are not sufficiently sensitive. The picrate test is neither specific nor sufficiently sensitive. The silver nitrate test is affected by acid and alkaline gases but it is sensitive.

Practical tests for hydrogen cyanide are especially important for use in vessel and other types of fumigation, first, for determining when a vessel or building is safe for habitation by its crew and by workers after the fumigation has been completed, and second, to establish the earliest moment when it is safe for a fumigating crew to enter a hold, compartment, vessel, or building for the purpose of further ventilation or to search for rats. Where the air workers breathe is to be tested for cyanide, sampling must be done at a point closely adjacent to the workers for the test to be of value and if there is any chance of the hydrogen cyanide concentration rising, sampling and testing should be performed at frequent intervals during the work.

Benzidine and Copper Acetate Test.[78] The benzidine and copper acetate test is one of the more widely used tests for the detection of hydrogen cyanide in atmospheres. It depends upon the production of a blue color with moist, freshly prepared benzidine and copper acetate test paper in the presence of hydrogen cyanide. This color is produced in periods varying from 3 to 30 seconds, depending upon the concentration of hydrogen cyanide.

Reagents. (1) Copper Acetate Solution.—Dissolve 2.86 g. of cupric acetate, $Cu(C_2H_3O_2)_2.H_2O$, in water and dilute to 1 liter. (2) Benzidine acetate solution.—Dilute 475 ml. of saturated benzidine acetate solution with 525 ml. of water.

Procedure.[79] Mix equal parts of the cupric acetate solution and the benzidine acetate solution just before using. Dip slips of filter paper into the mixed reagent and take into the compartment to be tested in closed tubes or vials. Open the tubes and note the time to the second. Upon exposure in an atmosphere of hydrocyanic acid, the test paper will show a color varying from a very faint to an intense blue, indicating from 20 to 80 mg. of hydrocyanic acid per cubic meter.

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[78] A. Sieverts and A. Hermsdorf, *Z. angew. Chem., 34,* 3 (1921).

[79] G. C. Sherrard, *U. S. Pub. Health Service, Reprint 1224* (1928).

The benzidine-copper acetate test requires that the test papers be read for a change in color after an exposure of from 7 to 10 seconds, which necessitates entering the compartment, hold, or building, if no auxiliary equipment is used, before making the test. This may be a dangerous procedure. An error of 3 seconds in reading the time factor might mean an error of 30 per cent or more in the accuracy of the test. The results must be read while the color is rapidly changing and the operator is in the presence of the cyanide. The color changes in widely varying concentrations of hydrocyanic acid are so slight that it requires considerable laboratory experience with known concentrations of hydrogen cyanide in order to make accurate determinations.

British Modification.[80,81] The official British modification of the benzidine-copper acetate test is the following.

Reagents. (1) Benzidine Acetate Solution.—Heat 2 to 3 grams of pure benzidine acetate in 100 ml. of water for 10 to 15 minutes at 80° C. with constant stirring. When cold, filter the mixture by suction. The filtrate will contain about 1 per cent of benzidine acetate.

(2) Copper Acetate Solution.—Dissolve 3 g. of cupric acetate, $Cu(C_2H_3O_2)_2.H_2O$, in 100 ml. of water.

Immediately before the test is made, mix 25 ml. of the benzidine acetate solution with 2 ml. of the copper acetate solution and stir well. The mixed reagent will not keep more than 15 minutes.

The test papers may be prepared from extra-thick white filter paper cut into strips 2 inches wide. Immerse them in the mixed reagent for 1 minute, drain, and allow to dry in a warm atmosphere. Cut off 1 inch at the top and bottom of the strip and discard. Cut the remainder of the strip into 3-inch lengths. The papers must be used immediately.

Procedure. Place a prepared test paper into a holder and attach to a hand exhausting pump which has a barrel of approximately 1.25 inch bore and a capacity of 125 ml. Make a preliminary test of the atmosphere by making 8 slow and steady strokes with the pump. Remove the paper and compare with the stains on standard charts.[80] In this way an estimate may be made of any concentration between 1 part in 10.000 and 1 part in 20.000 of air by volume, the latter being the maximum that can be inhaled for 1 hour without serious disturbance. If the stain indicates a concentration greater than 1 part in 20.000, a fresh paper is placed in the holder and further tests are made with 1, 2, 3, or 5 strokes of the pump; or if a concentration of less than 1 in 100.000 is indicated, a rough estimate of the concentration may be obtained by repeating the test with a greater number of strokes of the pump, until a stain equal to one of the standards is obtained. Comparison of the stains should be made in diffused daylight or with the use of a day light lamp.

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[80] *Dept. Sci. Ind. Research Brit., Leaflet 2* (1938).

[81] *Analyst, 63,* 658 (1938).

Methyl Orange-Mercuric Chloride Test.[79] This test depends on the change in color produced in a methyl orange-mercuric chloride test paper by hydrocyanic acid. The color changes from orange to pink. These test papers may be prepared in advance at a convenient place and will keep under proper conditions of humidity for as long as 30 days.

Reagents. (1) Mercuric Chloride Solution.—Dissolve 1.25 g. of mercuric chloride in 250 ml. of water.

(2) Methyl Orange Solution.—Dissolve 0.60 g. of methyl orange in 250 ml. of water.

Mix 10 ml. of mercuric chloride solution with 5 ml. of methyl orange solution and add 1 ml. of glycerol. Immerse strips of Whatman No. 40 filter paper into the mixed reagent and hang them up to dry in air which is free from any trace of acid. When dry cut the filter paper into strips $^{1}/_{4}$ inch wide and preserve in glass tubes protected from the light.

Procedure. Attach the test paper by means of a clip or other holding device to some type of line such as a fishing line and reel. Lower the test paper into the place to be tested. Withdraw at the end of 2 minutes. A definite pink color at the end of two minutes exposure indicates a dangerous concentration of hydrogen cyanide gas in the air unless the humidity is great enough to accelerate the reaction. The test can also be made by carrying a small vial into the place to be tested and noting the change in color at the end of a known period of time. The use of a line eliminates the need of masking, which is, of course, required when entering an unknown concentration of hydrocyanic acid. It is best to have two vials, one containing a strip of unaffected test paper, and the other containing a strip of paper with the pink danger color. Table 19

TABLE 19

Methyl Orange-Mercuric Chloride Test[79]

HCN per 1,000 cu. ft., grams	Proportion of standard[a]	Duration of test, minutes				
		0.5	1	1.5	2	3
6.7	1/10	Slight pink at edge	Faint pink	Definite pink	Red	Red
3.35	1/20	No change	Slight pink at edge	Faint pink	Definite pink	Red
1.675	1/40	No change	No change	Br. orange	Faint pink	Faint pink
0.8375	1/80	No change	No change	No change	Slight pink	Very faint pink
0.4187	1/160	No change	No change	No change	No change	No change
0.2093	1/320	No change	No change	No change	No change	No change

[a] The word standard indicates 2 ounces of HCN per 1,000 feet of air space.

shows the relationship of hydrogen cyanide concentration, color of test paper, and time of test.

Simultaneous Test.[82] Katz and Longfellow describe a series of three tests for the simultaneous testing of hydrogen cyanide. They use a dry picric acid test paper, which changes color from yellow to tan to brown; a wet guaiacum-copper test paper, which changes color from white to blue; and a wet phenolphthalin-copper test paper, which changes color from pink to bluish-pink, depending upon the hydrocyanic acid concentration. They estimate the quantity of hydrogen cyanide from the range of color with the aid of a color chart and the time required to yield the color.

The picrate papers may be prepared by dipping filter paper strips, 2 by $^{3}/_{4}$ inches into a solution containing 1 g. of picric acid and 10 g. of sodium carbonate dissolved in 100 ml. of water, and then drying the papers in room air. The papers may be prepared as much as 1 week in advance. The test paper is used dry and in the presence of hydrogen cyanide it changes color from yellow to tan to brown within a time period of 5 minutes, depending upon the hydrocyanic acid concentration.

The phenolphthalin [$C_{20}H_{16}O_4$] papers are prepared in the atmosphere to be tested by dipping a copper sulfate paper into a phenolphthalin solution. To prepare this solution, dissolve 20 g. of sodium hydroxide in 100 ml. of water; stir in $^{1}/_{2}$ g. of phenolphthalein dissolved in 30 ml. of alcohol; transfer to a 12-inch evaporating dish to prevent loss of forth; add 25 g. of 30–60-mesh aluminum powder; heat, and add water as required to continue the reaction; after 20 minutes to 1 hour, when the solution is colorless, filter with suction, dilute to 250 ml., and preserve. The solution may develop a light pink but this will not appear on the test papers. When used in the atmosphere to be tested the solution should be restoppered immediately. The test paper is used wet and changes color from white to pink to bluish-pink with the formation of phenolphthalein.

Guaiacum papers must be prepared in the atmosphere to be tested by dipping filter-paper strips of the aforementioned size previously wetted with a solution of copper sulfate, 50 mg. in 100 ml. of water, into tincture of guaiacum, 4 g. of guaiacum in 100 ml. of alcohol.

In making the simultaneous test with the three papers, the picrate paper is suspended first; while observing the picrate paper, the phenolphthalin paper is prepared and suspended; and while observing both of these tests, the guaiacum paper is prepared and suspended. The quantity of hydrogen cyanide is estimated from the times and color changes of the three test papers. These papers are affected by oxidizing agents and reducing agents in general and by chlorine, nitrogen peroxide smoke, ammonia, and formaldehyde in particular. Changes are inhibited by sulfur dioxide.

Phenolphthalin Field Method. This method[82a] is designed for the spot sampling of hydrogen cyanide in air and is based on the reaction devised by Katz and Longfellow as described on page 450.

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[82] S. H. Katz and E. S. Longfellow, *J. Ind. Hyg.*, *5*, 97 (1923–4).

[82a] Medical Division, Merck & Co., Inc., Rahway, N. J.

Reagents. Stock Solution (Solution *A*). Dissolve 0.166 g. of phenolthalin, $(C_6H_4OH)_2CHC_6H_4COOH$, in 75 ml. of ethyl alcohol. Dissolve 0.33 g. of copper sulfate, $CuSO_4.5H_2O$, in 100 ml. of water. Transfer both solutions to a 200-ml. volumetric flask and make to volume with water. This reagent will remain stable for at least a week if kept in a refrigerator.

Buffer Solution (Solution *B*). Dissolve 2.5 g. of trisodium phosphate, $Na_3PO_4.12H_2O$, in water and dilute to 1 liter.

Test Reagent. Dissolve 2 ml. of solution *A* in 98 ml. of solution *B*. The test reagent is stable for 8 to 24 hours after which time it may develop a slight color but this does not interfere with the sensitivity of the test.

Standard. Dilute 10 ml. of the test reagent to 50 ml. with solution *B* and add a small grain of sodium cyanide. The color developed is equivalent to that given by sampling the following volumes of air containing the designated concentrations of hydrogen cyanide.

Air sampled, ml.	Concentration HCN, ppm.	Time effect
2000	10	
1000	20	
500	40	
250	80	Maximum for 30 min.
125	160	Dangerous for 30 min.
75	320	Fatal in 5 min.

Procedure. Place 10 ml. of test reagent in a midget impinger tube and aspirate a known volume of air through it until the color matches the standard. Obtain the concentration of hydrogen cyanide from the volume of air sampled and the above table.

Chlorine, bromine, iodine, phenol, and high concentrations of hydrogen sulfide interfere with the test. If the air being sampled has a high acid concentration, the pH of the reagent should be checked after 1 liter of air has been sampled. This should be done by adding 1 drop of phenolphathlein indicator solution. The test reagent should turn red.

d. Determination

Pyridine-Pyrazolone Method.[83,84] By converting cyanide to cyanogen chloride with chloramine T and by the subsequent reaction of this cyanogen chloride with an aqueous pyridine solution containing 0.1 per

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[83] R. I. Nicholson, *Analyst, 66,* 189 (1941).
[84] J. Epstein, *Anal. Chem., 19,* 272 (1947).

cent of bis-pyrazolone and 3-methyl-1-phenyl-5-pyrazolone, a dye is formed which is stable for at least 0.5 hour at 25° C. and which follows the Beer-Lambert law between the limits of 0.2 and 1.2 micrograms of cyanide ion.

Reagents. Recrystallize commercial 3-methyl-1-phenyl-5-pyrazolone twice from 95 per cent ethyl alcohol, to obtain the product melting at 127–128° C.

To prepare bis-(3-methyl-1-phenyl-5-pyrazolone), dissolve 17.4 g. (0.1 mol) of recrystallized 1-phenyl-3-methyl-5-pyrazolone in 100 ml. of 95 per cent alcohol and add 25 g. (0.25 mol) of freshly distilled phenylhydrazine. Reflux the mixture for 4 hours. Filter the mixture while hot to obtain the insoluble portion, which is the bis-pyrazolone, and wash the precipitate several times with hot 95 per cent ethyl alcohol. The melting point should be higher than 320° C.

Pyridine-Pyrazolone Solution.—Mix 500 ml. of a saturated water solution of 3-methyl-1-phenyl-5-pyrazolone with 100 ml. of pure pyridine in which 0.1 g. of the bis-pyrazolone has been dissolved.

Standard Cyanide Solutions.—Dissolve 95 per cent sodium cyanide in water and analyze by the Liebig method (see page 455). Adjust the concentration of the solution to exactly 10 micrograms of cyanide ion per ml. and use this as a stock solution. Withdraw 2-, 4-, 6-, 8-, 10-, and 12 ml. aliquots of the stock solution and dilute to 100 ml. with water. These solutions contain 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 micrograms of cyanide per ml., respectively.

Procedure. Place 1 ml. of the unknown solution containing up to 1.2 micrograms of cyanide ion into a test tube and add 0.2 ml. of 1 per cent aqueous solution of chloramine T. Stopper the tube immediately and shake. After 1 minute add 6 ml. of the pyridine-pyrazolone reagent, stopper the tube, and again mix. After 20 minutes compare the optical density at 630 mμ with that of a blank and standards in a 1- to 1.5-cm. cell. A Coleman Universal spectrophotometer No. 11 with PC No. 4 filter is adequate. The standards can be used to set up a calibration curve and the concentration of the unknown can be obtained from that curve. The color is stable for at least 30 minutes after maximum development at room temperature.

Prussian Blue Test. This test is one of the most characteristic for hydrocyanic acid and cyanogen. However, unless special precautions are taken it is not sufficiently sensitive. It cannot be easily used in the field as a test and therefore has its main use as a laboratory test.

In making the test, an alkaline solution of cyanide is warmed with a few drops of a solution of ferrous sulfate. This converts the cyanide to ferrocyanide.

$$2KCN + FeSO_4 \longrightarrow K_2SO_4 + Fe(CN)_2$$
$$Fe(CN)_2 + 4KCN \longrightarrow K_4Fe(CN)_6$$

Ferrocyanide may in turn be detected by acidification and the subsequent addition of dilute ferric chloride solution, yielding a blue precipitate of ferric ferrocyanide:

$$3K_4Fe(CN)_6 + 4FeCl_3 \longrightarrow 12KCl + Fe_4[Fe(CN)_6]_3$$

It should be noted that the Prussian blue reaction is a time reaction and that excess ferric ion hinders the formation of the blue pigment.

Procedure. Pass the gas to be tested through a series of two or three gas bubblers containing a few ml. of 0.5 per cent potassium hyroxide solution to which a few drops of freshly prepared ferrous sulfate solution has been added. If the gas has been sampled in a gas collector, shake the gas in the collector with a few ml. of the dilute alkali containing the ferrous sulfate. After sampling is complete, if necessary sampling 100 liters of air, or sufficient time has elapsed to permit the hydrogen cyanide to be absorbed by the alkali, transfer the alkali solution to a beaker and heat to boiling, or allow to stand for at least 2 hours. This insures complete conversion to ferrocyanide. Cool, if necessary, filter off excess ferrous hydroxide, acidify slightly with hydrochloric acid, and add 1 drop of ferric chloride solution. In the presence of hydrogen cyanide, a blue color is formed.

Quantitative estimation may be made colorimetrically. Prepare a standard solution of potassium cyanide, 1 ml. of which is equivalent to 0.1 mg. of hydrogen cyanide. Dissolve 0.2411 g. of potassium cyanide in 1 liter of water. Dilute 100 ml. of this solution to 1 liter. One ml. of this solution contains 0.01 mg. of hydrogen cyanide. Prepare a series of control tubes containing from 0.02 to 0.1 mg. of hydrogen cyanide. Treat them exactly the same way the unknown is treated. Make the comparison after diluting to the same volume after 3 to 4 hours. A water blank should be run also.

An alternative color standard may be prepared by titrating an equal volume of water, slightly acidified, containing an equivalent quantity of ferric chloride, with potassium ferrocyanide solution, 3.1 g. per liter, until a match is obtained. One ml. of this solution is equivalent to 1 ml. of hydrogen cyanide or cyanogen at S. T. P.[85]

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[85] G. Lunge and H. R. Ambler, *Technical Gas Analysis,* Van Nostrand, New York, 1934.

For very small quantities of hydrocyanic acid, of the order of 0.00002 g. per ml., it is convenient to use the following procedure.[86] Add to the trapping solution or other test solution 2 drops of 10 per cent caustic soda, and evaporate nearly to dryness. Cool, add 1 drop of 2 per cent freshly dissolved ferrous sulfate, and leave in the cold for 10 to 15 minutes. Add 2 to 3 drops of concentrated hydrochloric acid, warm gently, and cool. If cyanide is present the liquid will show a blue color with careful dilution.

Test-Paper Method. Gettler and Goldbaum[86a] found that the sensitivity of the Prussian blue test could be enhanced by leading the hydrocyanic acid through an impregnated piece of filter paper held in a glass test paper holder equipped with ground flanges.

To prepare the test paper, dissolve 5 g. of hydrated ferrous sulfate in 50 ml. of water and filter to remove any insoluble residue. Immerse a single sheet of Whatman No. 50, smooth-glazed, acid- and alkali-treated filter paper into the ferrous sulfate solution by suspending it from a clamp and allow to dry in the air. Dip the dried ferrous sulfate impregnated filter paper into a 20 per cent solution of sodium hydroxide and again allow to dry in the air. Cut circular pieces of paper having the same diameter as the ground-glass flanges of the holder. The papers are stable for several weeks if stored in a dark, cool place.

Procedure. Pass the air being tested through the test paper held by the test paper holder by aspiration or suction. Place samples (2 g.) being tested for cyanides in a 50-ml. aeration tube, add 3 ml. of water, and acidify with dilute sulfuric acid. Connect one end of the aeration tube with one end of the holder and place the aeration tube itself in a beaker containing water at 90° C., the surface of the water in the beaker being no higher than that of the liquid in the tube. Apply suction at the maximum rate for 5 minutes. Remove the test paper from the holder and place it in a dilute solution of hydrochloric acid (1:4) to dissolve any iron hydroxides which may mask the color. Wash the test paper with water and dry. A blue stain indicates the presence of cyanide, the intensity being proportional to the amount of cyanide present.

Thiocyanate Method.[87] This method depends upon the conversion of cyanide to cyanate by boiling an alkaline solution of cyanide with ammonium polysulfide until the solution is colorless or down to dryness.

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[86] G. D. Lander and A. E. Walden, *Analyst, 36,* 266 (1911).

[86a] A. O. Gettler and L. Goldbaum, *Anal. Chem., 19,* 270 (1947).

[87] C. K. Francis and W. B. Connell, *J. Am. Chem. Soc., 35,* 1624 (1913).

$$KCN + (NH_4)_2S_2 \longrightarrow (NH_4)_2S + KCNS$$

The subsequent addition of acid and ferric ion will produce the red color of ferric thiocyanate, a soluble nonionized substance.

In order to eliminate the interference of alkali and acid, the cyanate may be extracted from the dry residue obtained by evaporation of the test solution, with 3 successive portions of acetone.[88] The combined acetone layer is evaporated and the residue is dissolved in water and transferred to a Nessler tube. Then 2 ml. of 0.5 per cent ferric chloride solution is added and the color produced is matched against standards treated the same way.

Procedure.[89] Pass a known volume of the air to be tested through a series of absorption bubblers containing about 15 ml. of 0.5 per cent alkali solution, at the rate of about 1 cubic foot per hour. Transfer the contents of the collectors to a volumetric flask and make to volume. Transfer an aliquot portion to a porcelain evaporating dish with the aid of a pipette. Add 1 ml. of ammonium polysulfide solution, and evaporate slowly to dryness. Dissolve the residue in a small volume of water, add 3 ml. of a 10 per cent solution of cadmium nitrate solution, and filter into a Nessler tube. Add 2 ml. of 0.5 *N* sulfuric acid. Prepare a series of standards containing from 0.003 to 0.02 mg. of hydrogen cyanide by transferring suitable aliquots of a standard potassium cyanide solution to porcelain evaporating dishes. Add 10 ml. of 0.5 per cent potassium hydroxide solution to each dish. Evaporate to dryness and then proceed as detailed for the unknown. Adjust the level in all the tubes to the same height. Add 2 ml. of 10 per cent ferric chloride solution. Compare the color produced at the expiration of $^1/_2$ hour.

Silver Nitrate Method.[90] The well-known Liebig method for determining hydrocyanic acid in air consists in absorbing it in dilute sodium hydroxide solution and titrating with standard silver nitrate solution. The reaction may be expressed by the equation:

$$2NaCN + AgNO_3 \longrightarrow NaAg(CN)_2 + NaNO_3$$

Absorb the hydrocyanic acid in 100 ml. of 2 per cent sodium hydroxide solution, add 5 ml. of 2 per cent potassium iodide solution, and titrate with standard silver nitrate solution containing approximately 3 g. of silver nitrate per liter. The volume of the gas sampled should be adjusted to provide enough hydrocyanic acid, when it is present, for a satisfactory titration and should be bubbled through the trapping liquid at the rate of about 1 liter per minute.

[88] M. O. Johnson, *J. Am. Chem. Soc.*, *38*, 1230 (1916).
[89] A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases*, Service to Industry, Hartford, 1936.
[90] H. L. Cupples, *Ind. Eng. Chem., Anal. Ed.* *5*, 50 (1933).

In this method of analysis the addition of potassium iodide increases the sharpness and reliability of the end point, which is indicated by the first permanent turbidity of the solution. The end point is somewhat difficult to see unless the illumination is favorable. Daylight is more satisfactory than ordinary artificial light. The end point is sharp when the titration is performed in semidarkness, with a condensed beam of light passing through the solution in a generally horizontal direction. Satisfactory results may be obtained by the use of a focusing flashlight, or the more powerful beam from a microscope illuminator. With such illumination a slight excess of silver nitrate produces a distinct Tyndall effect.

The end point of this titration may be obtained with greater accuracy by means of a photronic photoelectric turbidimeter, which works on the principle of determining the beginning and the degree of turbidity.[91]

Bicarbonate-Iodine Method.[92,93] Hydrocyanic acid in sodium carbonate solution absorbs iodine with the formation of cyanogen iodide:

$$\mathrm{NaCN} + \mathrm{I_2} \longrightarrow \mathrm{NaI} + \mathrm{CNI}$$

Upon acidification of this mixture, iodine is released. No other gas behaves this way.

Cupples[94] modifies this method by absorbing the hydrocyanic acid in a 2 per cent solution of sodium carbonate, with subsequent titration with standard iodine solution. The iodine solution must be added slowly, with very efficient stirring for the results to be consistent and in agreement with those of the silver nitrate method. Unless precautions are taken it is comparatively easy to incur errors of 5 to 10 per cent.

Satisfactory analyses may be made by absorbing the hydrocyanic acid in about 100 ml. of 2 per cent sodium carbonate solution, adding 10 ml. of 10 per cent potassium iodide solution and 5 ml. of 2 per cent starch solution, then titrating with standard iodine solution with efficient stirring.

Ammonia Method.[95] Small amounts of hydrocyanic acid may be determined quantitatively by use of a general characteristic reaction of *alkyl nitriles*, that is, the hydrolysis of these nitriles with either acid or alkali to form the alkyl acids or their salts and ammonia or its salts. Hydrocyanic acid follows this reaction for it is the nitrile of formic acid:

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[91] E. T. Bartholomew and E. C. Raby, *Ind. Eng. Chem., Anal. Ed.*, 7, 68 (1935).

[92] G. E. Seil, *Ind. Eng. Chem., 18,* 142 (1926).

[93] G. Lunge and H. R. Ambler, *Technical Gas Analysis*, Van Nostrand, New York, 1934.

[94] H. L. Cupples, *Ind. Eng. Chem., Anal. Ed., 5,* 50 (1933).

[95] N. Gales and A. Pensa, *Ind. Eng. Chem., Anal. Ed., 5,* 80 (1933).

$$HCN + HCl + 2H_2O \longrightarrow HCOOH + NH_4Cl$$
$$HCN + KOH + 2H_2O \longrightarrow HCOOK + NH_4OH$$

The hydrolysis must be carried out in a closed system, for otherwise the hydrocyanic acid would be volatilized with acid hydrolysis and the resultant ammonia with alkaline hydrolysis.

For analytical purposes it is best to hydrolyze by autoclaving in a glass autoclave at 140–150° C. for 30 minutes in an acid solution. The Leiboff[96] urea apparatus is suitable. The Leiboff autoclave is a resistant glass ampoule of about 35 ml. capacity with an inner-seal ground-glass rod so that the autoclave may be sealed and suspended from the glass rod at the same time. With care, satisfactory results can be obtained with medicinal ampoules if made of resistant glass.

Procedure. Transfer the test solution, which consists of the hydrocyanic acid trapped in 0.1 *N* sodium hydroxide solution, to a volumetric flask. Make to volume. Transfer a 25-ml. aliquot with the aid of a pipette to the autoclave or ampoule and add 5 ml. of concentrated hydrochloric acid. Seal the ampoule, if used. Heat slowly in an oil bath and maintain the temperature between 140 and 150° C. for 30 minutes Cool, break the ampoule, if used, and transfer with the aid of water to a 50-ml beaker. Evaporate slowly, almost to dryness, on a hot plate. This is done to remove excess acid. Dilute with water, transfer to a Nessler tube, and add 5 ml. of Nessler's reagent (page 364). Compare the resulting color as directed in the method for ammonia (page 365). When an ampoule is used instead of the autoclave, cool the ampoule in an ice bath before the addition of hydrochloric acid and seal it immediately.

2. *Cyanogen*

Cyanogen, $(CN)_2$, may occur in coal gas and is often associated with hydrogen cyanide. Its degree of hazard is relatively the same as hydrogen cyanide. It is so closely allied to that compound both in its physiological and chemical action that they are generally estimated together as hydrocyanic acid.

Cyanogen may be differentiated from and estimated in the presence of hydrocyanic acid by means of silver nitrate solution acidified with about 2 drops of dilute nitric acid for each 10 ml. of 0.1 *N* silver nitrate solution. This solution will absorb only the hydrocyanic acid and will not absorb the cyanogen. Since the cyanogen is not absorbed, it will pass out with the effluent gas and thus may be estimated by one of the other methods previously detailed for hydrocyanic acid such as the ferrocyanide method or the thiocyanate method. The hydrogen cyanide trapped by the silver nitrate solution may be estimated in the usual way.

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[96] S. B. Leiboff and B. S. Kahn, *J. Biol. Chem., 83,* 347 (1929).

3. Cyanogen Chloride and Cyanogen Bromide

Cyanogen chloride, CNCl, is a colorless, highly volatile liquid. It boils at 12.5° C., solidifies at −6.5° C., and has a specific gravity of 1.2 and a vapor density of 2.1. One volume of water will dissolve 25 volumes of cyanogen chloride at 20° C. It is soluble in organic solvents like ether and alcohol but decomposes rather readily in alcohol. Cyanogen chloride polymerizes into cyanuryl chloride, $(CNCl)_3$, which is physiologically inactive. This cyanogen compound is used industrially as a fumigant, as a warning agent in other fumigants, and in the manufacture of organic chemicals. During World War I it was used alone and in combination with arsenious chloride.

Cyanogen chloride, in addition to being a systemic poison, is a lachrymator and is used as a warning agent in commercial fumigation with hydrogen cyanide. Concentrations of the order of 0.0025 mg. per liter of air induce copious watering of the eyes. A concentration of 0.5 mg. per liter is intolerable and exposure to a concentration of 0.4 mg. per liter for 10 minutes is probably a lethal exposure.

Cyanogen bromide, CNBr, is a solid which forms transparent crystals melting at 52° C. It has a sharp penetrating odor, boils at about 61° C., and has a specific gravity of 1.9 and a vapor density of 3.6. It is not readily soluble in water but dissolves more readily in alcohol and the usual organic solvents. This compound is used industrially in the synthesis of organic chemicals. In World War I it was used in mixtures with bromoacetone dissolved in benzene. This mixture was known as Campiellite by the French.

It is fairly strong lachrymator and irritant as well as systemic poison; 0.006 mg. per liter will affect the conjunctiva and the mucous membranes of the respiratory tract. The limit of intolerance is 0.085 mg. per liter, although some authorities give a lower concentration as the intolerable limit. It can cause death.

Sodium Sulfide Test Paper. Aspirate the air to be tested through a paper soaked in a saturated sodium sulfide solution and used moist.

$$CNBr + Na_2S \longrightarrow NaCNS + NaBr$$

Add 1 drop of concentrated hydrochloric acid, followed by a few drops of 1 per cent ferric chloride solution. A red color due to ferric thiocyanate indicates the presence of a hydrogen halide.

Since both cyanogen chloride and bromide are very volatile, it is best to carry out this test on the original sample rather than by absorbing the gases on activated charcoal or silica granules before applying the test.

Cyanogen bromide reacts with hydrogen sulfide, hydrogen iodide, and sulfur dioxide to yield hydrogen cyanide. This may be detected as explained. Cyanogen chloride undergoes a similar reaction with hydrogen iodide but its reaction with hydrogen sulfide is more complex, since thiocyanic acid is also formed. Cyanogen bromide will give the Prussian blue reaction but cyanogen chloride must be converted to hydrogen cyanide before this test can be applied. If sodium hydroxide solution is added to a sample and it is boiled, the cyanogen halides yield ammonia.

Cyanogen chloride can be detected and estimated by the pyridine-pyrazolone method detailed in a previous section in this chapter.

4. Calcium Cyanamide

Calcium cyanamide, NC.NCa, also known as "Nitrolime" and "cyanamide" (cyanamide is actually $NC.NH_2$), is made by heating calcium carbide, CaC_2, in an atmosphere of nitrogen at 1000° C.

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

It is now being manufactured in large quantities for use as a fertilizer and also for the production of ammonia and explosives. It is a hazard in the industries mentioned above.

a. Physiological Response

Calcium cyanamide powder is caustic. It may cause severe abscesses and cellulitis on sweating skins. Deep-seated ulcers may occur in the mucous membranes of the nose, mouth, and throat. The symptoms exhibited in poisoning by this substance are transitory redness of the face, irritation of the nose, throat, and skin, flushing of the skin, headache, marked congestive hyperemia of the face and upper third of the body, accelerated and deepened respiration, rapid pulse, vasodilation with lowered blood pressure, and a feeling of giddiness. These symptoms are intensified in workers who have consumed alcohol. The duration as well as the severity of the poisoning are proportional to the amount and time of exposure to the substance and the condition of the subject. Attacks, according to McNally[96a], last from $^1/_2$ to 2 hours.

b. Detection and Determination

The amount of calcium cyanamide dust in a working atmosphere can be determined by an appropriate method described in Chapter V, such as filtration or electrostatic precipitation. The simplest method of detection is to trap the dust in water, heat, and test for ammonia. The simplest method of determination is to trap the dust in a sulfuric acid solution and then run nitrogen according to the Kjeldahl-Gunning-Arnold method for protein.[96b]

[96a] W. D. McNally, *Toxicology,* Industrial Medicine, Chicago, 1937.

Calcium cyanamide is hydrolyzed with *hot* water forming ammonia:

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3$$

Hence it can be estimated by direct nesslerization after distillation as described for ammonium chloride (page 365). It is well to bear in mind that small amounts of complex organic compounds may be formed during the hydrolysis.

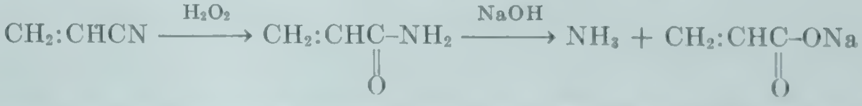
5. *Acrylonitrile*

Acrylonitrile, $CH_2{:}CHCN$, vinyl cyanide, propenenitrile, is a colorless liquid which boils at about 78–79° C. It has a specific gravity of 0.807 at 20° C., a refractive index of 1.3884 at 25° C., a flash point (open cup) at 32° F., a lower explosible limit of 3.05 per cent by volume, and an upper explosible limit of 17.10 per cent. About 7 g. of acrylonitrile are soluble in 100 ml. of water at 20° C. and this material dissolves about 3 per cent of water at the same temperature. Acrylonitrile is miscible with alcohol, ether, and chloroform and is soluble in nearly all the common organic solvents.

Toxicological studies of this substance show that acrylonitrile is a compound whose toxicity is comparable to a molecular equivalent of hydrogen cyanide.[97,98] The recommended maximum allowable concentration for this compound is 20 parts of acrylonitrile per million parts of air by volume.

Determination

The concentration of acrylonitrile[99] in air can be determined by trapping the compound in concentrated sulfuric acid, hydrolyzing it in strongly alkaline solution with hydrogen peroxide, and estimating the quantity of ammonia liberated by customary methods.



$$CH_2{:}CHCN \xrightarrow{H_2O_2} CH_2{:}CH\underset{\overset{\|}{O}}{C}\text{–}NH_2 \xrightarrow{NaOH} NH_3 + CH_2{:}CH\underset{\overset{\|}{O}}{C}\text{–}ONa$$

[96b] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products*, Van Nostrand, New York, 1945.

[97] H. C. Dudley and P. A. Neal, *J. Ind. Hyg. Toxicol.*, *24*, 27 (1942).

[98] H. C. Dudley, T. R. Sweeney, and J. W. Miller, *J. Ind. Hyg. Toxicol.*, *24*, 255 (1942)

[99] G. W. Peterson and H. H. Radke, *Ind. Eng. Chem., Anal. Ed.*, *16*, 63 (1944).

Sampling. Prepare two traps analogous to that of Figure 102A from 0.25-inch test tubes and glass tubing, using stoppers and tubes as the outlet. Add sufficient glass beads to the traps to form a 1-inch column; add 2 ml. of concentrated sulfuric acid to each trap. Connect the traps in series and immerse in an ice bath. Draw air through the traps at a maximum rate of 0.4 liter per minute, measuring the rate of flow at a maximum with a rotameter or equivalent device. Sample sufficient air to provide about 6 mg. of acrylonitrile.

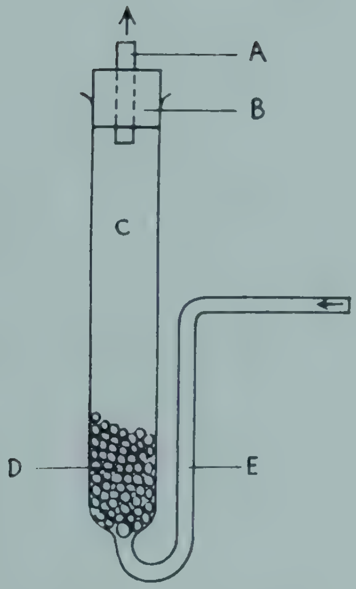


Fig. 102A. Absorption trap[99]: (A) glass outlet tube; (B) one-hole rubber stopper; (C) 0.25-inch test tube; (D) glass beads; and (E) glass inlet tube.

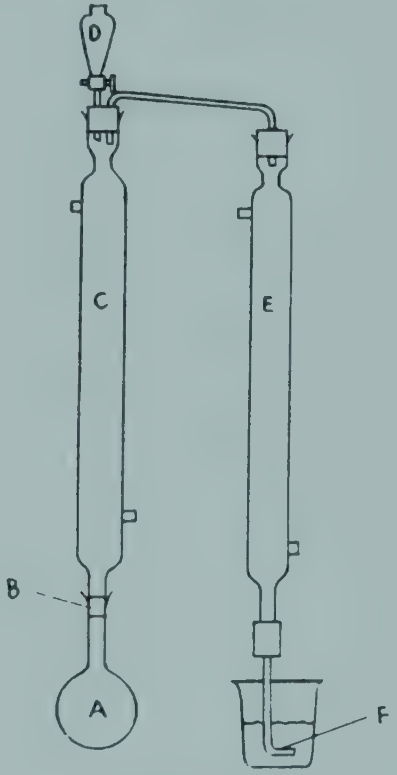


Fig. 102B. Apparatus for determination of acrylonitrile: (A) 200-cc. balloon flask; (B) ground-glass joint; (C) reflux condenser; (D) separatory funnel; (E) No. 2 condenser; (F) sintered-glass bubbler.[99]

Wash the sample into a 200-ml. round bottom flask and add 0.2 g. of copper acetate to act as an inhibitor and thus prevent polymerization. Attach the flask to the apparatus shown diagrammatically in Figure 102B.

Procedure. Pipette 25 ml. of 0.025 N sulfuric acid into the titration beaker and dilute with water until the bubbler adapter is covered by 0.5 inch of water. Make the sample alkaline by the addition of 50 ml. of 50 per cent sodium hydroxide solution through the separatory funnel. Wash the residual sodium hydroxide solution from the separatory funnel and reflux condenser with 10 ml. of water and 20 ml. of 30 per cent hydrogen peroxide solution, adding the latter slowly. Reflux gently for 30 minutes. Drain the water from the reflux condenser and distill over one-half the volume in the flask. Wash the second condenser with water and titrate the excess sulfuric acid with 0.01 N sodium hydroxide solution, using methyl red as the indicator.

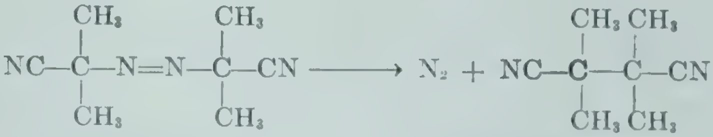
Calculate the concentration of acrylonitrile by use of the following formula:

$$\text{Ppm.} = (25.00N_A - N_BV_B) \times \frac{1}{V_S} \times C$$

where: N_A = Normality of H_2SO_4
V_B = ml. of NaOH used in the titration
N_B = Normality of NaOH
V_S = liters of air sampled
C = 22,400 corrected to sampling pressure and temperature

6. *Tetramethylsuccinonitrile* [100]

In the preparation of sponge rubber a "blowing" compound, azo-*bis*-isobutyronitrile, is used. This compound, known under the name Porofor-N, occurs in colorless crystalline needles or prisms melting at 105° C. with the evolution of gaseous nitrogen and the formation of tetramethylsuccinonitrile:



$$NC-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-CN \longrightarrow N_2 + NC-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CN$$

Azo-*bis*-isobutyronitrile

Tetramethylsuccinonitrile

Tetramethylsuccinonitrile, often termed TSN, crystallizes in plates melting at 169° C. It sublimes readily. At 28° C., its volatility is 69 ppm. equivalent to 0.38 mg. per liter; at 63° C., its volatility is 1025 ppm. or 5.07 mg. per liter; and at 100° C., its volatility is 7820 ppm. or 34.8 mg. per liter. Tetramethylsuccinonitrile is very soluble in alcohol and ether and is almost insoluble in water and petroleum ether. This nitrile has almost no odor.

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[100] R. N. Harger, *personal communication,* 1948.

a. Physiological Response

Experiments with rats indicate that tetramethylsuccinonitrile is a toxic material. Rats exposed to a concentration of 90 ppm. exhibited their first convulsion after 1.5–2 hours and were dead in 3 hours or less. Rats exposed to concentrations of 5.5 ppm. exhibited their first convulsion in 27–31 hours and were dead in 31 to 46 hours. With rats, guinea pigs, rabbits, and dogs given parenterally a 1 per cent solution of tetramethylsuccinonitrile in 20 per cent alcohol (kept warm to prevent precipitation of the test substance), the fatal dose was about 25 mg. per kilo.

Harger points out that the toxic action of this nitrile appears to be different from that of many other nitriles in that thiosulfate proved to be a poor antidote. Barbiturates proved adequate for the control of convulsions. Those barbiturates, however, which have a short or medium period of action will relieve the symptoms for a time, after which they may reappear causing the death of the animal. This action indicates that tetramethylsuccinonitrile is slowly detoxified, or eliminated, by the body.

b. Determination

The method of Harger and Hulpieu[101] depends on the observation that tetramethylsuccinonitrile is quantitatively absorbed from air in cold, concentrated sulfuric acid. The nitrogen in the compound is readily converted to ammonia by heating and the ammonia formed may be estimated by direct nesslerization or by nesslerization after concentration by steam distillation. Other nitrogenous compounds would also yield ammonia by this method but in the Porofor-N method for the manufacture of sponge rubber, none of the other nitrogenous compounds are sufficiently volatile to introduce errors. For related determinations in which other volatile bases are present, such bases may be removed by the introduction of a tube containing solid tartaric acid between the scrubber tube and the air source. A similar guard tube containing soda lime will remove volatile nitrogenous acids.

Apparatus. Gas Scrubber.—This is a Pyrex tube, Figure 102C about 18 mm. O. D. and 6 inches long sealed at the bottom and having an inlet and an outlet tube each about 1/2 inch long and 6 mm. O.D., sealed into the top. The inlet tube passes through the top of the scrubber tube and extends almost to the bottom of this tube where it ends in a bulb perforated with 3 small holes. Both inlet and outlet tubes are straight, with no bends.

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[101] R. N. Harger and H. R. Hulpieu, Indiana University School of Medicine, 1948.

Ammonia Standard. Weigh out 0.471 g. of C.P. ammonium sulfate, dissolve in 5 per cent sulfuric acid, make up to 100 ml. with this acid, and mix well. This stock solution contains 1 mg. of ammonia N per ml. It will keep well for at least one year. Prepare the standard ammonia solution by diluting 6 ml. of the stock solution with 500 ml. of water, adding 20 ml. of concentrated sulfuric acid, diluting to 1 liter with water, and mixing well. This standard contains 0.006 mg. of ammonia N per ml. It keeps quite well, for one or two weeks.

Procedure. Fill a 25-ml. burette with concentrated sulfuric acid. Introduce the tip of the burette through the outlet tube of the gas scrubber and run in 3 ml. of the sulfuric acid. Connect the inlet of the scrubber to the place where the air is to be analyzed, using a length of small glass tubing if necessary. The joint between this tube and the bubbler inlet should be glass-to-glass. Connect the outlet of the gas scrubber to a flowmeter which, in turn, is connected to a suitable source of suction. Conduct the air through the apparatus at a measured rate, which should not exceed 1 liter per minute, for the desired length of time.

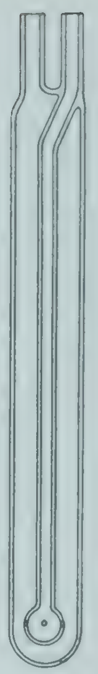

Fig. 102C. Gas scrubber.[101]

At the end of the aeration disconnect the scrubber tube and draw the acid up into its inlet tube two or three times to dissolve any sublimate caught in this tube. Place the scrubber tube in a clamp and close the inlet tube with a rubber sleeve plugged with a glass bead. Heat the acid in the scrubber tube over a microburner with a flame about $^1/_2$ inch high until the fumes of sulfuric acid appear. If tetramethylsuccinonitrile has been caught the fluid will turn dark. If darkening occurs remove the flame and cool in air for 1–2 minutes. With a small glass tube constricted at the end, introduce 3 drops of the hydrogen peroxide through the outlet tube. Shake the scrubber tube to mix. Continue the addition of the peroxide until the sulfuric acid is water-clear. Heat again over the microburner to drive off the excess of water and peroxide and boil gently for two minutes; remove the flame and allow the tube to cool in air for five minutes. Place the scrubber tube in cold water for two minutes. When the tube contents are cold, connect a source of water to the inlet tube and run in water until the tube is almost filled. Transfer the contents of the tube to a 100-ml. volumetric flask using a small funnel to prevent loss of fluid. Pour the contents of the scrubber tube out through the outlet tube, rinsing the tips of the scrubber tube inlet and outlet with a stream of water from a wash bottle. Rinse out the scrubber tube twice more with distilled water adding the rinsings to the flask. Make up to the mark with distilled water and mix well.

To determine the ammonia formed, place a measured aliquot, not to exceed 3.3 ml., in a test tube and add water to give a total volume of exactly 5 ml. In a second test tube place 5 ml. of the standard ammonia solution containing 0.006 mg. of ammonia N per ml. Add 3 ml. of Nessler solution (page 364) to each tube. Mix and read in a suitable colorimeter. If one of the tubes is much darker than the other a different aliquot must be used. If the solution from the digestion is too weak to read in the colorimeter it should be concentrated as follows: Transfer 80 ml. of the solution to a Kjeldahl flask connected in the usual way to a condenser, the end of which dips into a little water containing 1 ml. of 5 per cent sulfuric acid. Introduce some glass beads or a piece of boiling stone into the Kjeldahl flask. Make the Kjeldahl flask contents strongly alkaline by adding 6 ml. of 50 per cent sodium hydroxide solution. Connect the Kjeldahl flask, mix the contents, and distill over about 40 ml. Transfer the distillate quantitatively to a clean Kjeldahl flask, add a glass bead, and boil off most of the water. Dilute the residue in the flask with water to a volume of 10 or 20 ml. and nesslerize an aliquot of this concentrated solution.

Calculation. The 5 ml. of standard used contains 0.03 mg. of nitrogen, which is equivalent to 0.146 mg. of tetramethylsuccinonitrile. The formula, therefore, is:

$$0.146 \times \frac{\text{Reading of standard}}{\text{Reading of unknown}} \times \frac{100}{\text{Volume of solution used}} = \text{Milligrams of tetramethylsuccinonitrile}$$

If crystals of tetramethylsuccinonitrile are caught in the tube leading from the air source to the scrubber tube these must be carefully washed out with concentrated sulfuric acid, made up to an exact volume with this acid, and the solution, or an aliquot of it, analyzed in the same manner as the contents of the scrubber tube. For digesting this solution, use a test tube containing a glass bead to prevent bumping.

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CHAPTER XII

General Methods for the Determination of Combustible and Solvent Vapors

At the beginning of the twentieth century there were scarcely a dozen industrial organic solvents of any importance. Among these were the benzine and benzene groups, certain alcohols, esters, and related compounds such as acetone. With the needs of World War I and the vast expansion in the use of nitrocellulose, cellulose acetate, synthetic resin, and plastic products came the need and development of commercial organic solvents on a tremendous scale.

The question of the poisonous nature of these solvents was, in the developmental stages, scarcely considered with regard to the more important considerations of fire and explosion hazard. In this period hundreds of organic compounds of a greater or lesser poisonous nature, particularly those of a noninflammable character, have been developed for industrial and commercial purposes and have found their way not only into large and small industrial plants but into the home as well. Of these hundreds, about 300 are in common use.

The ideal solvent, one which is at the same time nonpoisonous, noninflammable, and so is not an explosion hazard, and which is an excellent industrial solvent has not as yet been discovered.[1] Every material which dissolves fats and oils is in a physiological sense active and consequently every good organic solvent is, under certain circumstances, poisonous. The only nonpoisonous solvent is still water,[1] and one can drown in that.

1. Physiological Effects of Industrial Solvents

The volatile solvents enter the body chiefly through the respiratory passages, but appreciable quantities may be ingested or absorbed through the intact skin. When harmful substances are inhaled, they pass into the general circulation and are distributed to the heart and the central nervous system with a rapidity second only to that which occurs when they are injected into the veins. They can produce either a general toxic action without harm to the respiratory tract or a mixed effect, being generally toxic and locally irritant. A few irrespirable vapors act so violently in the upper respiratory system and lungs that their general toxic effects are secondary considerations. With few exceptions, all volatile solvents if inhaled in sufficient concentration for a sufficient length of time are detrimental to health.[2]

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[1] K. B. Lehmann and F. Flury, *Toxikologie und Hygiene der technischen Loesungsmittel,* Springer, Berlin, 1938.

Flury[1] classifies the physiological action of the industrial solvents under five main headings:

(1) General nerve poisons without other distinctly specific poisonous effects; to this group belong the primary alcohols (with the exception of methyl alcohol), ethers, aldehydes, ketones, and certain esters, and benzine.

(2) Lung poisons or irritants, that is, those substances which induce the phenomenon of inflammation in the tissues with which they come into immediate contact; the principal representatives of this group are the esters of the methyl series and formic acid esters.

(3) Blood poisons; benzene and its derivatives are the chief examples; however, the glycols are also in this group.[3,4]

(4) Liver poisons and metabolic poisons; to this group belong principally the chlorinated hydrocarbons.

(5) Kidney poisons; representative of this group are tetrachloroethane and the glycols.

Flury[1] also places in a special group such specific nerve poisons as carbon disulfide and trichloroethylene.

The physiological action can also be considered from the point of view of type of action. These are irritant, narcotic or anesthetic, suffocating, and functional injury to the metabolism. The solvents do not belong to any one type but obviously fall into a number of groups.

The effects of inhalation of vapors can be local or remote. They can be acute or chronic. The effects of inhalation are more severe than that of swallowing because they are rapidly taken up by the blood stream, pumped all over the body, and thus make themselves felt more readily than would otherwise be possible.[5]

The main physiological action of the more important industrial solvent groups and a few organic gases are summarized briefly in the following paragraphs.

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[2] W. J. McConnell, *J. Am. Med. Assoc., 109,* 762 (1937).

[3] L. Greenburg, M. R. Mayers, L. Goldwater, W. J. Burke, and S. Moskowitz, *J. Ind. Hyg. Toxicol., 20,* 134 (1938); *N. Y. State Ind. Bull. 17,* 269 (1938).

[4] C. E. Parsons and M. E. Parsons, *J. Ind. Hyg. Toxicol., 20,* 124 (1938).

[5] P. Drinker, *Ind. Med., 4,* 253 (1935).

Saturated Hydrocarbons. The saturated hydrocarbons of the aliphatic group are relatively harmless from the toxicological point of view, the lower homologues being less harmful than the higher ones. Methane and ethane are simple asphyxiants; propane and butane have, in addition, anesthetic properties, while the hydrocarbons from pentane up are narcotic, convulsive, and irritant. Hexane and heptane are the most dangerous.

Unsaturated Aliphatic Hydrocarbons. These compounds from ethylene to heptylene have simple asphyxiant and anesthetic properties. Acetylene may also be included in this group.[6]

Cyclic Hydrogenated Hydrocarbons. The cyclic hydrogenated hydrocarbons are more potent than the open-chain hydrocarbons but are less toxic than the aromatic hydrocarbons. Cyclohexane has about the same toxicity as benzine but has a stronger narcotic action. They have their principal effect on the central nervous system.

Aromatic Hydrocarbons. The aromatic hydrocarbons are much more poisonous than the aliphatic group. They are, in general, blood poisons. Toluene and xylene are, according to Flury,[1] more poisonous than benzene but because they are less volatile there is less danger from chronic poisoning. More recent work, however, has shown that toluene is about one-eighth as poisonous as benzene.

Chlorinated Hydrocarbons. The chlorinated hydrocarbons are among the most poisonous of the solvents. They are liver and metabolic poisons. They have a marked effect on the nervous system because they are lipoid solvents, and they act as heart depressants.[2] The physiological effect of the chlorinated hydrocarbons is discussed in some detail in Chapter XV.

Alcohols. The alcohols show a regular dependence of narcotic action on their physical constants with anesthetic power increasing with increasing molecular weight. Butyl and amyl alcohol have in addition a slight irritant action and some degree of poisonous action on the protoplasm. Secondary alcohols are stronger narcotics than the primary alcohols. With the exception of methyl alcohol, which has poisonous properties of its own, the toxicity of the alcohols is comparatively small.

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[6] Y. Henderson and H. W. Haggard, *Noxious Gases,* Reinhold, New York. 1927.

Glycols and Alcohol-Ethers. Formerly the glycols and the alcohol-ethers were considered relatively harmless but increasing experience has shown that they are more dangerous than has been supposed. They are principally blood and kidney poisons. The action of the glycols is discussed more fully in Chapter XVI.

Aldehydes and Ketones. The aldehydes are primarily irritant but they also have some narcotic action. Formaldehyde is poisonous and a concentration of 10 parts per million is considered the threshold of a safe working atmosphere. Acrolein is also a powerful poison.

The ketones are narcotic and are markedly stimulating to the respiratory center. They range in toxicity from isophorone, for which the maximum allowable concentration is 25 parts per million, to acetone, for which the recommended value is 500 parts per million.

Ethers. The ethers are powerful narcotics acting rapidly on the central nervous system. They are also slightly irritant. They can be dangerous if inhaled in large quantities.

Acids. The acids act on the skin causing burns and dermatitis. Inhalation of the acid fumes may cause irritation of the mucous membranes.

Esters. The action of the esters varies widely from the mildly anesthetic and irritant properties of ethyl acetate to the very poisonous, irritant, and vesicant action of methyl sulfate and the esters of formic acid. The formic acid esters are powerful irritants, especially the chlorinated ones.

With increase in molecular weight the relative toxicity of the esters increases, but because of decrease in volatility the actual danger decreases. In addition to volatility, solubility in water and the ease of saponification are factors which have their effect on the degree of toxicity of the esters.

Aniline and Coal Tar Derivatives. These substances are blood poisons and are in general much more poisonous than the solvents mentioned above.

2. *Organic Solvents as Agents Causing Dermatitis*

Organic solvents cause dermatitis in three ways. First, by dissolving and removing the fatty and sebaceous content of the skin, resulting in dryness and cracking. Thin, dry skins are more likely to be affected than thick, oily ones. Second, by actually dissolving the superficial keratin layer and causing erythema and vesiculation. Third, by an allergic reaction in which contact with small amounts may cause severe generalized dermatitis. Some of the industries in which dermatitis attributable to solvents is relatively common are the airplane (use of dopes), painting (use of thinners), degreasing, and printing and lithographing industries.

The following are among the principal groups[7] of solvents causing dermatitis:

(1) Petroleum derivatives: benzine, kerosene, gasoline, naphtha, ligroin, Varsol, Stoddard solvent;

(2) Coal-tar derivatives: coal-tar naphtha, solvent naphtha, benzene, toluene, cymene, xylene, tetralin, decalin;

(3) Turpentine group: turpentine, wood spirit, pine oil, pine needle oil, oil of spike, terpineol, rosin spirit, tar spirit;

(4) Alcohols: methyl, ethyl and its denaturants, propyl, butyl, amyl, benzyl, and cyclohexyl;

(5) Chlorinated hydrocarbons: methylene chloride, chloroform, carbon tetrachloride, dichloroethylene, trichloroethylene, tetrachloroethane, pentachloroethane, perchloroethylene, monochlorobenzene, dichlorobenzene;

(6) Esters: methyl acetate, ethyl acetate, butyl acetate, methyl formate, ethyl formate, butyl formate, amyl formate;

(7) Ketones: acetone, methyl acetone, ethyl methyl ketone, methycyclohexanone;

(8) Glycols;

(9) Nitroparaffins: nitromethane, nitroethane, 1- and 2-nitropropane;

(10) Carbon disulfide.

3. Toxicity of Organic Solvents

The toxicity of organic solvents depends on many factors, among which are solubility, vapor pressure, volatility, chemical activity, concentration, etc.; because of these many factors it is very difficult to classify the solvents according to their degree of toxicity. In a very broad classification they can be placed into three groups, although these groups are by no means hard and fast and consequently overlap considerably in individual instances.[8]

In the first group, which consists of the solvents least harmful from an industrial point of view, either because of very low vapor pressure or because they are of low inherent toxicity, may be placed the straight-chain saturated hydrocarbons, ethyl alcohol, ether, the middle-range esters of acetic acid, acetone, and, among the chlorinated hydrocarbons, dichloromethane, monochloroethylene, and tetrachloroethylene. Flury includes the glycols in this group because of their low volatility but that is a doubtful classification. They should be placed, at least, in the second group.

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[7] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939); *Ind. Hyg. Newsletter, Supplement 1*, Nov. 1947.

[8] K. B. Lehmann and F. Flury, *Toxikologie und Hygiene der technischen Loesungsmittel,* Springer, Berlin, 1938.

The second group consists of those solvents which are of higher toxicity and contains by far the largest proportion of the known industrial solvents. Among these may be mentioned the amyl derivatives, most of the chlorinated hydrocarbons, trichloroethylene, the homologues of benzene, chlorobenzene, and the hydrogenated cyclic hydrocarbons.

The third group consists of those substances which are strongly poisonous, not only under test conditions but also under industrial conditions. Among these are the methyl linkages such as methyl alcohol, methyl chloride, dimethyl sulfate, tetra- and pentachloroethane, benzene, and carbon disulfide.

The relative degree or order of toxicity of the solvents may be seen by reference to Tables 3 and 5, Appendix, which give the safe working limits of a number of the more important solvents.

4. Gases in Manholes and Sewers

The hazards in sewers, sewage treatment plants, and manholes are those associated with the hazards attributable to all gases in common, namely, (1) inflammable gases, (2) a diminution of oxygen with subsequent asphyxiation if such an atmosphere is entered, (3) poisonous gases. Because of the predominance of the first two classes some mention of the composition of these gaseous mixtures is appropriate at this point. Table 20 summarizes the composition of gases found in sewers, sewage tanks, and manholes. It must be stressed, however, that the composition of gases found in sewers and manholes varies widely. The most common components of sewer and sewage gases are carbon dioxide, methane, ethane, oxygen, hydrogen, and hydrogen sulfide. In manhole gas, in addition to those gases mentioned, illuminants and carbon monoxide are also present. These are generally attributable to leakage of utility and manufactured gas. Other gases found occasionally are ammonia from refrigerator leaks, sulfur dioxide from burning insulation, and phosphine, which is sometimes generated in sludge-digestion tanks. Sludge-digestion gas consists principally of methane (65 to 80 per cent of the total volume) and carbon dioxide (20 to 35 per cent). Hydrogen, nitrogen, hydrogen sulfide, and oxygen are minor components.

TABLE 20
Composition of Gases Found in Sewers, Sewage Tanks and Manholes

Gas	Explosibility	Source[a] in manholes	Paris[b] sewer, %	Composition Imhoff[c] sewage-sludge tanks, %	Boston[d] manholes, %
Ammonia	Explosive	Refrigerating plants	...	...	...
Benzene	Explosive	Motor vehicles, storage tanks	...	...	...
Carbon dioxide	Nonexplosive	Combustion products	2.01	3.3–29.4	0.0–8.3
Carbon monoxide	Explosive	Mfg. fuel gas, flue gas, motor exhaust	...	...	0.0–34
Nitrogen	Nonexplosive		81.21	2.9–23.3	19.5–85.6
Gasoline	Explosive	Motor vehicles, storage tanks	...	...	0.0–0.1
Hydrogen	Explosive	Artificial fuel gas, electrolysis of water	...	0.0–8.2	0.0–44.1
Hydrogen sulfide	Explosive	Sewer gas, coal gas	2.99	0.0–0.1	...
Methane and ethane	Explosive	Natural gas, mfg. gas, sewer gas	...	63.0–84.2	0.1–25.4
Sulfur dioxide	Nonexplosive	Burning insulation	...	...	...
Unsaturated hydrocarbons	Explosive	Mfg. fuel gas	...	...	0.0–2.5
Oxygen	...	Air	13.79	0.0–1.2	3.7–20.9

[a] S. H. Katz, E. G. Meiter, and J. J. Bloomfield, *U. S. Bur. Mines, Rept. Invest. 2710* (1925).
[b] Taylor, *Medical Jurisprudence,* London, 1897.
[c] R. R. Sayers, *U. S. Pub. Health Repts. 49,* 144 (1934); C. C. Mommon, *Eng. News, 71* 760 (1914); A. M. Bushwell and S. I. Strickhouser, *Ind. Eng. Chem., 18,* 407 (1926).
[d] G. W. Jones, J. Campbell, and F. M. Goodwin, *U. S. Bur. Mines, Rept. Invest. 3213* (1933).

These hazards are discussed by Sayers,[9] Ash,[10] and the Sub-Committee on Occupational Hazards of the Federation of Sewage Works Associations.[11]

As an illustration of the explosibility of these gases the range exhibited by the gases obtained from Imhoff sewage-sludge-digestion tanks may be considered. This range extends from a lower inflammable limit of 5.3–8.3 to an upper inflammable limit of 16.0–19.3.

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[9] R. R. Sayers, *U. S. Pub. Health Repts. 49,* 144 (1934).
[10] S. H. Ash, *Sewage Works J., 5,* 662 (1933).
[11] *Manual of Practice, 1* (1944).

5. General Methods for the Determination of Solvent Vapors

While this chapter is primarily concerned with general methods for the determination of solvent vapors, the organic gases like methane, ethane, etc., which act in some measure like the solvents and are closely allied to them, will also be included in the discussion.

There are instances of industrial processes in which a single solvent or diluent is used, for instance, in the degreasing of metal parts by trichloroethylene, but there are many more in which mixtures of solvents and diluents are used. Thus, in all likelihood, whenever ethyl alcohol is used in a preparation it is accompanied by its denaturant. Cellulose ester lacquers are complex mixtures of cellulose ester, plasticizer, gum resin, pigment, solvent, and diluent. The volatile fraction consisting of solvent and diluent generally comprises 75 per cent, and the remaining components 25 per cent. The volatile fraction may be a complex mixture of hydrocarbons, alcohols, esters, ketones, etc., all of which contribute their share of the vapor contaminant of the air.

While it may be difficult to analyze these solvent vapors in order to determine the relative proportion they assume, it is often unnecessary to do this because for the purpose of ascertaining whether a health or fire hazard exists, it may be sufficiently adequate and useful to determine the total amount of solvent or combustible vapor in the air. The value of the general methods for the estimation of solvent vapors is based on this. In other instances, it may be valuable to estimate the concentration of the most dangerous contaminant and to be guided by that determination.

The general methods for the estimation of solvent vapors in air are based on the physical chemical properties of these solvent vapors. Among the more important properties used are those of vapor pressure, absorption of radiant energy, index of refraction, conductivity, combustibility, and adsorption on some agent. The properties of combustibility and adsorption are more generally used for the determination of vapor concentration than the others.

a. Analysis of Solvent Mixtures

It is beyond the scope of this book to discuss the analysis of solvent mixtures or even of the mixture of vapors of solvent mixtures in any detail.

Briefly the analysis of a cellulose acetate lacquer is as follows. The ratio of volatile to nonvolatile substance is obtained gravimetrically by heating a weighed portion of the mixture in a tared dish in a thermostatically controlled oven. The nonvolatile component consists of a mixture of cellulose ester, gum resin, plasticizer, and pigment.

Adequate laboratory fractionating columns[11b] equivalent to 50 theoretical plates have been devised and serve to fractionate many types of solvent mixtures.

The volatile components may be separated from the nonvolatile components by distillation in a hood over a hot air, water, or oil bath. It may be necessary to use a vacuum setup.

The hydrocarbons are absorbed in fuming sulfuric acid or may be separated by fractional distillation.

Methyl and ethyl alcohol may be separated by their solubility in calcium chloride solution, from which, after dilution, they can be recovered by distillation. Alcohols, in general, may be esterified with acetic anhydride and the acetyl value determined as detailed on page 624. Esters may be estimated by saponification (page 655). Butyl and amyl alcohols and esters can be determined by the methods detailed in Chapter XVI (page 656 *et seq.*). Ketones may be ascertained by the hydroxylamine method (page 686).

Goldman[12] has outlined methods for the analysis of solvents which are valuable guides. Details of the identification methods are given in the text.

Steam distill *paints and lacquers* to yield a two-phase distillate, namely, an aqueous and a nonaqueous phase. Distill *rubber cements* under vacuum. Extract the distillate with water to obtain an aqueous and a nonaqueous phase. Neutralize *alkaline rubber accelerators* with hydrochloric acid and then distill under vacuum.

Aqueous Layer. Distill the aqueous layer and cut into three fractions, 74° C., 74–80° C., and 80–100° C. The first cut at 74° C. may contain acetone, methyl alcohol, and methyl acetate. Determine methyl acetate by saponification. Estimate acetone by the iodoform reaction and back titration of excess iodine. Obtain the quantity of methyl alcohol by difference.

[11b] F. Todd, *Ind. Eng. Chem., Anal. Ed., 17,* 175 (1945).

[12] F. H. Goldman, presented at an Industrial Hygiene Seminar, *Ind. Hyg. Div., Bur. State Services. U. S. Public Health Service,* St. Louis, May, 1944.

The second cut may contain ethyl alcohol and ethyl acetate. Determine ethyl acetate by saponification and ethyl alcohol by difference.

The third cut may contain butyl alcohol, small amounts of butyl acetate, and water-soluble ketones. Salt out the third fraction with excess sodium chloride, remove the oily layer, and add it to the nonaqueous portion.

Nonaqueous Layer. Dry the water-insoluble fraction over anhydrous potassium carbonate. Separate the acetates by fractionation using a simple still head. Take the first cut at 107° C. giving ethyl acetate, etc., the second cut 107–127° C. giving butyl acetate, etc., the third cut 127° C. giving amyl acetate, etc. Saponify a portion of each fraction and calculate the acetate content.

Reflux a portion of the water-insoluble solvents with phenylhydrazine and distill up to 175° C. The loss in weight represents the ketones removed.

Extract the distillate consisting of alcohols, acetates, benzene, toluene, xylene, and gasoline with hydrochloric acid. This treatment leaves only benzene, toluene, xylene, and gasoline in the nonaqueous layer. Wash the nonaqueous layer, dry, and distill. It is generally possible at this point to decide which of the solvents is present. If gasoline is present, nitrate the mixure and distill to 175° C. The loss in weight represents the aromatic solvents.

Butyl alcohol, amyl alcohol, and fusel oil are found by difference. Concentrated sulfuric acid may be used instead of concentrated hydrochloric acid, in which case subject the sulfuric acid solution to distillation for the recovery of the dissolved solvents.

Fractionation. The scheme of separation outlined above is generally applicable to most of the solvent mixtures which are encountered with the exception of those consisting of mixtures of paraffins, naphthenes, and aromatics. In order to simplify this type of analysis, it is customary to group the naphthenes and paraffins together. This is particularly convenient when the naphthene content is low and the aromatic content is high. Another simplification can be secured by grouping toluene and xylene together. From an industrial hygiene point of view this is adequate since their maximum allowable concentrations are the same. Benzene must be estimated separately.

Apparatus. A typical still consists of a boiling flask, a column, a still head, a thermometer, and an adaptor. It is necessary to heat both the still pot and the fractionating column. A convenient boiling flask is a round-bottom, 1-liter flask with a ₸ 24/40 joint, heated electrically. A Glas-col heater with a Variac is suitable for this purpose. The still head may be a total condensation, variable take-off device and may or may not have a cold spot. Almost any type of adaptor may be used to collect the distillate. The column is preferably equipped with ₸ joints and is packed with glass helices. It may either be vacuum jacketed or inserted in a length of tubing of wider diameter so that it is surrounded by an air space. The column is conveniently wound with resistance wire and the heat may be controlled with a Variac. A thermometer is attached to the side of the column to record the column temperature. Adequate apparatus is commercially available.

Procedure. Dry the liquid to be distilled either with anhydrous potassium carbonate or sodium sulfate. Weigh the sample and record all the fractions obtained on a weight basis. Heat the still pot so that boiling takes place as vigorously as possible without causing flooding of the column. Use a boiling rod or chips to prevent bumping or overheating. Heat the column to within two degrees of the thermometer reading at the take-off. Boil the liquid and allow to reflux until the lowest temperature is reached at which this will occur. Open the still-head stopcock partially and collect a fraction. Collect the distillate at a rate which depends upon the rate of refluxing. A 10:1 or 20:1 ratio may be desirable.

There are various methods which may be used for collecting the fractions. In one method start with 1 liter of solvent mixture and take off 10-ml. fractions irrespective of temperature changes. Each fraction then represents about 1 per cent of the original sample on a weight basis.

In another method (which involves taking less fractions and is more convenient when the components are known), take fractions according to temperature differences, such as at 2-degree intervals.

A simpler method depends upon the availability of a refractometer. Check the refractive index of the distillate as the boiling point rises. Take new fractions when the refractive index begins to change appreciably. As a variation of the refractive index method, take fractions when schlieren effects are noted as drops of distillate touch the distillate previously collected.

Construct boiling point, refractive index, and specific gravity curves. Determine the composition of the solvent mixture from these constants. For such constants, see Ward and Kurtz.[13]

[13] A. L. Ward and S. S. Kurtz, *Ind. Eng. Chem., Anal. Ed., 10,* 559 (1938).

6. *Explosive Limits*[14]

The reaction of a gas or vapor with the oxygen of the air, resulting in progressive combustion or propagation of flame, occurs only when the concentration of the gas or vapor in the air is within certain limits. When the concentration of the flammable gas or vapor is outside these limits, local combustion may occur at the source of ignition but there is no actual propagation of flame, and the combustion ceases on removal of the source of ignition. The minimum and maximum concentrations of a gas or vapor in air which, if ignited, propagate flame independently of an external source of ignition (heat) are known as the lower and higher flammable or explosive limits. There must also be present a minimum concentration not only of flammable gas but of air or oxygen for the propagation of the flame. These limits are usually expressed in terms of percentage of vapor or gas in air by volume. The explosibility of some of the more common gases is given in Table 2, Appendix.

The difference between the lower and upper flammable or explosive limits of a gas or vapor is known as the explosive range. Thus the lower limit of methane is 5 per cent of methane in air by volume (5.6 per cent according to some authorities), while the higher limit of explosibility is 15 per cent of methane in air (13.5 per cent according to some authorities). By difference there is an explosive range of approximately 10. There must be at least 12.1 per cent of oxygen present for methane to explode.[15–17]

7. *Detectors*

Combustion-Type Detector. *Jones Gas Detector.* This gas detector was developed by G. W. Jones[18] of the U. S. Bureau of Mines. It is designed to show, in field use, the approximate explosive content of an atmosphere in confined spaces. It can also show the presence of an atmosphere deficient in oxygen. It can indicate whether an atmosphere is within the explosive range, below the lower explosive limit, or above the upper explosive limit.

It consists essentially of a bomb in which is inserted a spark plug, and to which is attached a pressure gauge.

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[14] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

[15] H. F. Coward and G. W. Jones, *U. S. Bur. Mines, Bull. 279* (1939).

[16] G. W. Jones, *U. S. Bur. Mines., Tech. Paper 450* (1929).

[17] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines, Miners' Circ. 33* (1938)

[18] G. W. Jones and G. St. J. Perrott, *U. S. Bur. Mines, Rept. Invest. 3109* (1931).

This apparatus can be used not only for the detection of methane, since it does not indicate methane alone, unless methane is the only combustible gas present, but also for many combustible gases and vapors which form explosive mixtures in air, such as illuminating gas, blast-furnace gas, hydrogen, naphtha, gasoline, alcohol, and some cleaning solvents.

The Burrell methane detector, another combustion-type gas indicator, is described on page 503.

Some detectors operate on the principle that practically all gases containing hydrogen and carbon or hydrogen, carbon, and oxygen produce approximately the same number of calories of heat per unit volume, if burned at the lower explosive limit. Thus the combustion of 100 ml. of alcohol, benzine, gasoline, propane, etc., burned at the lower explosive limit, produces approximately 50 calories. Hence an indicator depending upon the calories produced will give similar indications for the combustion of these substances.

U. C. C. Methane Detector. This detector is essentially a portable Wheatstone bridge one arm of which includes a heated platinum filament. This bridge, with its meter adjusted to zero in air, becomes unbalanced when in an atmosphere containing a combustible gas because of the effect of the burning of the gas on the surface of the heated filament, which causes an increase in the temperature and resistance of the filament proportional to the percentage of the gas present.

The change in resistance of the filament causes a deflection of the needle of the meter in the bridge circuit. The meter scale, graduated from 0 to 7 per cent, is calibrated to show directly the percentage of methane present. This instrument will not work efficiently in atmospheres deficient in oxygen.

M. S. A. Detectors. There are a number of M. S. A. combustible-gas detectors[19] that are used for the detection of methane and other combustible gases. The essential feature of one of these detectors is the autopotentiometer circuit. This is a balanced circuit for the potential drop across the detector unit and part of the potentiometer rheostat equals the potential drop across the compensating unit and the remaining part of the potentiometer rheostat. When these two potential drops are equal, the meter pointer of the instrument is at zero. A change of the resistance of the detector filament, due to the burning of methane or some combustible gas, causes a change in the potentials of the two halves of the circuit and the indicator pointer moves in response to this change.

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[19] Mine Safety Appliances Co., "Explosimeter"; "Combustible Gas Indicator."

Another M. S. A. detector works on the principle of the Wheatstone bridge. The instrument is used in the following manner. By operating a small piston-type pump or by squeezing an aspirator bulb, a sample of the atmosphere to be tested is drawn through a length of sampling line into the instrument. Sampling line of practically any length may be used, with no lag in the indicator reading except the time required to draw the sample through the line.

In the instrument the gas sample flows over a hot platinum wire which forms a part of a balanced electrical circuit, current for which is provided by two small dry-cell batteries. This detector unit is balanced against the filament of a small electric light bulb burning in an inert atmosphere, or against another platinum-wire filament. Combustion of gases on the surface of the detector filament creates an increase in its resistance, thus causing the electrical circuit to become unbalanced. This unbalancing of the circuit causes a deflection of the pointer of the meter proportional to concentration of gas in the atmosphere being tested. The concentration of gas may be read directly on the meter, which is graduated in per cent of the lower explosive limit.

Some combustible-gas indicators, while very useful for explosible gases, are not sufficiently sensitive to be used for very low concentrations of certain combustible vapors. Thus the lower explosive limit for benzene is 1.4 per cent by volume (14,000 parts per million). The lowest combustible-gas indicator reading of some devices is 2 per cent, which is equivalent to about 280 parts per million of benzene vapor in air. This is more than 5 times the concentration considered the safe working limit for benzene.[20]

A benzene-combustible-gas indicator[21] has been developed which is much more sensitive than the types mentioned above and is capable of indicating 20 parts of benzene per million of air. It is equipped with a drying agent which may tend to remove certain types of organic vapor.[22]

The difficulties encountered in adjusting the zero of this device are discussed by Setterlind.[22a] To overcome these difficulties Setterlind places activated carbon or silica gel in the purge canister and the customary calcium chloride in the test canister.

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[20] S. Moskowitz, *N. Y. State Ind. Bull. 16,* 502 (1937).

[21] Mine Safety Appliances Co., "Benzol Indicator."

[22] *Am. Pub. Health Assoc., Yearbook, 1939–40,* 92.

[22a] A. N. Setterlind, *Ind. Hyg. Newsletter, 8,* No. 12, 9 (1948).

Davis Vapotester.[23] As shown by Figure 103, the electrical circuit is a balanced Wheatstone bridge in which two legs are incandescent platinum filaments. Both of these filaments are housed in a single cell block having two chambers. One chamber is completely sealed and houses the comparison filament. The other chamber is so arranged that air or gas mixtures can be drawn through it and houses the active, or analyzing, filament. This chamber is fitted with flashback or flame arrestors, to prevent propagation of flame out of the chamber.

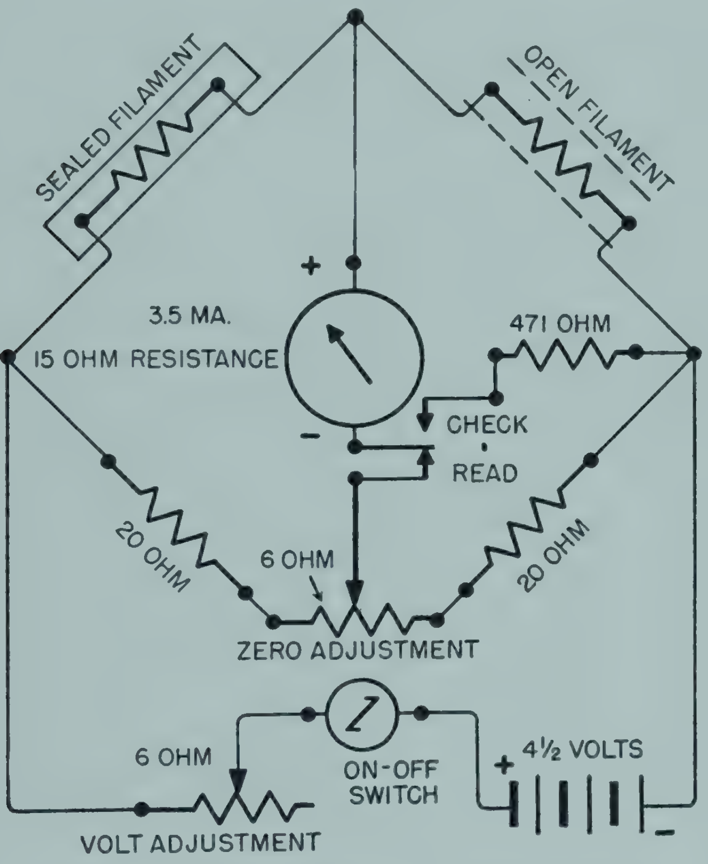
SEALED FILAMENT
OPEN FILAMENT
+
3.5 MA.
15 OHM RESISTANCE
471 OHM
CHECK
READ
−
20 OHM
6 OHM
20 OHM
ZERO ADJUSTMENT
6 OHM
ON-OFF SWITCH
+
4½ VOLTS
−
VOLT ADJUSTMENT

Fig. 103. Wiring diagram of Davis Vapotester.

When a combustible gas-air mixture is drawn through this open chamber, it ignites on the surface of the analyzer filament, increasing its temperature. This increases the resistance of one leg of the bridge and unbalances the circuit so that current flows through the meter. The amount of current which flows through the meter is directly proportional to the percentage of explosible or combustible gas (by volume) present up to the lower explosive limit. The dial of the meter is calibrated against explosibility and is read in terms of percentage of the lower explosive limit.

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[23] Davis Emergency Equipment Co., Newark, N. J.

8. Adsorption Methods

a. Adsorption by Silica Gel[23,24]

Air suspected of contamination by gases and vapors may be sampled by passing a measured volume of air, freed from water and carbon dioxide, over proper and adequate absorbents and adsorbents. The air is then passed over silica gel in weighed U-tubes, which adsorbs the organic vapors. The U-tubes are reweighed and the additional weight is considered to be due to adsorbed organic vapors.

Apparatus. The adsorption trains consists of five 150-mm. glass-stoppered Pyrex U-tubes with one male and one female ground-glass interchangeable connection on the side arms of each tube. The first tube contains a mixture of about 90 per cent Ascarite and 10 per cent Desicchlora in the first limb and Desicchlora in the second limb. The second and third tubes are filled with 8- to 16-mesh silica gel. The fourth tube is similar to the first and the fifth is also similar but reversed, that is, the Desicchlora is in the first limb and the Ascarite-Desicchlora mixture in the second limb. Each limb of each tube is topped with a plug of glass wool. No lubricant is used on the ground-glass connections. Two tubes of silica gel are used because two tubes are necessary for efficient adsorption of organic vapors since silica gel is less efficient than an equal volume of activated charcoal for that purpose.[24]

The function of the first tube is to remove water and carbon dioxide from the air being sampled and tested. The two tubes of silica gel absorb the organic vapors from the air. The fourth tube absorbs the carbon dioxide and water lost by the silica gel as the dry, carbon dioxide-free air passes over it. The last tube is a safety tube used to prevent the absorption of moisture and carbon dioxide if air should back into the train. The entire train is mounted on sponge rubber and is encased in wood for transportation in the field.

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[23] G. V. Pigulevskii and A. K. Yabovtzeva, *Arb. wiss. Forsch-Sekt. Leningrad* (Abt Arbeitsschutzes 1 Pt.), *2*, 306 (1927); *Chem. Abstracts*, *25*, 4491 (1931).

[24] S. Moskowitz and W. J. Burke, *N. Y. State Ind. Bull. 17*, 168 (1938).

If several successive tests are to be run, duplicate sets of the three center tubes of the train are necessary. The initial tube will remove the water and carbon dioxide from a considerable volume of even very humid air before requiring refilling. The silica gel is replaced when it has adsorbed 10 per cent of its weight of contaminants although commercial silica gel can be used beyond that point without a breakdown.

If benzine is the volatile vapor, the used silica gel can be freed from the benzine by heating it to 100° C. and passing purified air through it for $^1/_2$ hour.

Procedure. To make a test of an atmosphere, rub the second, third, and fourth tubes with a soft cotton cloth, allow them to come to equilibrium with the laboratory air, and weigh to apparent constant weight. At the same time, fill another tube with either silica gel or Ascarite and Desicchlora and treat it in a similar fashion. This tube is used as a control. Assemble the train, place it in its rack, and take it to the place where the air is to be sampled. Draw air through the train at a rate of 20 liters per hour. Place a flowmeter in the line between the train and the suction pump or equivalent device to measure the volume of air sampled. The length of time during which the air is sampled depends on the concentration of the contaminant expected. The usual sampling time is 1 to 2 hours.

On returning to the laboratory with the train and its sample, open for a moment a stopcock on each of the second and third tubes containing the silica gel, on the fourth tube which contains Ascarite and Desicchlora, and on the control U-tube, in order to permit equilization of pressure to take place. Close the stopcocks. Rub each tube as before, allow them to come to equilibrium with the laboratory air, and weigh to apparent constant weight. If the control tube has changed no more than 1 mg., no correction is applied, otherwise the correction needed for the blank is applied to the weight of each of these tubes. The net change in weight of the three tubes in milligrams is divided by the volume of air in liters drawn through the apparatus to give the concentration of contaminants in milligrams per liter of air.

Where only a single contaminant is present in the air, its concentration as milligrams per liter can be calculated[25] in terms of parts per million of air as explained in Chapter III, or from Table 1, Appendix. When several contaminants are present and the rapid and complete evaporation of the solvent occurs, the concentration of each contaminant in the air will tend to be proportional to its concentration in the liquid evaporated. When, however, incomplete evaporation occurs, an approximation of the proportion in the air of each volatile component can be made by calculations from its vapor pressure and the effect on its vapor pressure by the other components.

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[25] A. C. Fieldner, S. H. Katz, and S. P. Kinney, *U. S. Bur. Mines, Tech. Paper 248* (1921).

Laboratory determinations with known amounts of solvents, using this system of adsorption, have shown that the maximum error is ±3 milligrams. Taking a 2-hour sample, which is equivalent to 40 liters of air, and adsorbing a substance whose molecular weight is 100, the maximum error becomes less than 20 parts per million.[24] This error may be reduced by using a longer sampling time.

b. Adsorption on Equilibrated Activated Charcoal[26]

An apparatus that can be used for field determinations consists essentially of a tube containing 8-mesh Ascarite and 20-mesh calcium chloride for the removal of acid vapors and moisture and an activated charcoal tube for the adsorption of solvent vapors. All parts of the train should be constructed by Pyrex or other heat-resistant glass and should be joined by means of Ŧ glass-to-glass connections. By avoiding all rubber connections in the train before the adsorption tube, errors, arising from absorption of solvent vapor by the rubber, can be eliminated. Such absorption may cause results to be low under certain conditions and high under other conditions.

The activated charcoal tubes can be constructed from No. 15 Ŧ, outer cone glass-to-glass connections, the unfinished ends of which are drawn down and fused onto a short piece of 7-mm. glass tubing bent at a right angle to the larger tube. This assists in holding in place a small plug of glass wool which supports the activated charcoal and also facilitates connecting the tube to the suction apparatus by means of rubber tubing. All ground-glass connections should be lubricated with a thin film of graphite, which may be conveniently applied with a soft lead pencil. The inner tube is inserted into the outer cone and the graphited surfaces are rotated against each other. In this manner the connections are made gas-tight without involving errors which result from the use of petrolatum or similar lubricants.

The charcoal tubes are filled with 8-mesh activated charcoal, previously dried in a constant-temperature oven at 150° C., in the following manner[27] (see page 96). Clamp the adsorption tube and a small funnel in a vertical position with the funnel stem centered in the tube 15 cm. from the apex to the designed height of the charcoal. The adsorbent is poured in with a spoon, a few grains at a time, so that no grains have a free fall through the orifice of the funnel. The time for filling a tube of 2 cm. diameter to a height of 10 cm. should not be less than 1.5 minutes, nor should the tube be tapped at any time. Air should be drawn through the tube at least five times during filling by quickly turning the stopcock between the tube and a 5-gallon suction bottle for 1–2 seconds and quickly closing. This procedure precludes the presence of fines which might otherwise be drawn from the tube during sampling and might constitute a serious source of error.

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[26] W. A. Cook and A. L. Coleman, *J. Ind. Hyg. Toxicol.*, *18*, 194 (1936).

Equilibration of the Charcoal Adsorption Tubes. The tubes prepared as directed above are equilibrated by drawing clean air through them at a rate of 1 liter per minute. The train for cleaning and drying the air consists of (1) concentrated sulfuric acid in gas-washing bottles for removal of most of the moisture; (2) 8-mesh Ascarite and 20-mesh calcium chloride contained in drying tubes for removal of acid vapors and any residual moisture, and also any acid spray carried over; (3) 8-mesh activated charcoal also contained in ordinary drying tubes for removal of any organic vapors which may be present in the laboratory air. After the air is drawn through the above train, it is drawn through the activated-charcoal sampling tubes. The rate of flow through these tubes is maintained at 1 liter per minute by flowmeters connected between each sampling tube and the source of suction.

In the initial equilibration after the tubes are first prepared, it is usually necessary to draw the purified air through the charcoal adsorption tubes for 24 hours. The charcoal tubes are then removed from the train, ground-glass interchangeable stoppers are inserted, and the tubes are wiped and weighed as directed below. The weighed tubes are replaced in the equilibration train and air is drawn through for another 30 minutes. If the deviation in weights before and after this run is less than 0.5 mg., the tubes are ready for use, otherwise the equilibration must be continued until apparent constant weight is obtained.

For weighing, wipe the tubes vigorously with old linen for 60 seconds and obtain the weight just 3 minutes after wiping commenced. It is advantageous to use a similarly wiped and equilibrated adsorption tube as a tare.

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[27] A. C. Fieldner, C. G. Oberfell, M. C. Teague, and J. N. Lawrence, *Ind. Eng. Chem.*, *11*, 519 (1919).

Procedure. Obtain the weight of a stoppered, wiped, air-equilibrated charcoal adsorption tube. Place the tube in its sampling train in the vicinity where the sampling is to be performed and pass a measured volume of the atmosphere to be tested through the tube at a rate of 20–30 liters per hour. After sampling is finished, disconnect the tube from the train and restopper. Allow time for temperature equilization and adjustment, wipe as before, and weigh as directed above. The gain in weight is attributed to the adsorbed solvent vapor. The gain in weight divided by the volume of the air used for sampling gives the concentration of the solvent vapor per unit volume.

c. Adsorption and Distillation

Adsorption methods can be used in other ways than gravimetric determination as detailed in the preceding sections. In general the atmosphere to be tested can be passed over activated carbon, which is heated with or without steam, to distill the adsorbed vapors, and the distillate is subsequently analyzed. Higher benzene derivatives require superheated steam at about 300° C.

Commercial devices[27a,27b] have been developed in Europe for the estimation of solvent vapors like those arising from coking operations which are based on the adsorption of the vapor on activated carbon, releasing the adsorbed vapors by heating at 250–300° C. and subsequent condensation of the vapor.

As representative of these methods, for example, a mixture of acetone and ethyl alcohol vapors can be adsorbed on activated carbon, the vapors can be driven off by heating the carbon, and after subsequent condensation can be estimated by the methods detailed in the text. In an analogous manner, a mixture of chlorinated hydrocarbons can be adsorbed, the activated carbon can then be steam distilled, and the mixture identified by the tests described in Chapter XV.

A variation of the adsorption and distillation method is the *adsorption and extraction method.* For instance, the vapors of tetralin can be adsorbed on activated carbon. The latter is extracted with benzene and the tetralin can be separated from the benzene by fractional distillation.

[27a] R. Kattwinkel, *Glückauf, 67,* 1409 (1931).
[27b] A. Simon, *Gas- u. Wasserfach, 79,* 361 (1936).

9. *Physical Chemical Methods*

a. The Gas Interferometer

The gas interferometer is a delicate optical instrument designed to compare the refractive indexes of two specimens of gas or vapor, one of which is a gas of known refractivity. The refractive index of a substance is the reciprocal of the relative velocity with which light passes through that substance, the speed of light through a vacuum being arbitrarily established as "1". A ray of light passing from a less dense to a denser medium is bent toward the normal, that is, its speed will be less through the denser medium and therefore it will have a higher refractive index. By comparison of the index of refraction of the atmosphere of an industrial environment with the index of refraction of a standard, say normal air, an estimate of the concentration of the contaminants may be made.[28,29]

In the interferometer described by Patty,[30] light from an incandescant filament passes through each of two cells 50 cm. in length. After passing through the cells, the light then combines to form interference fringes. When the composition of the gas in the two tubes differs, the optical paths through the tubes differ and the interference fringes are displaced to the right or left. Two beams passing outside the cells form similar fringes in fixed position, serving as a reference point from which to measure the displacement. The optical path of the beam through the gas under observation is equalized with the beam through the standard gas by changing the angle of a glass compensator plate placed in its path. This plate is attached to a lever arm. Its position is adjusted by a micrometer screw, which covers an arbitrary scale of 0. to 30 and makes contact approximately at right angles with the movable arm when it is at zero. Each revolution of the screw, which is equivalent to 1 on the scale, is divided into 100 parts.

Interferometer readings must be converted into concentration of vapor in air. This can be done by either of two methods: (1) by calibration

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[28] S. Moskowitz, *N. Y. State Ind. Bull. 16,* 502 (1937).

[29] G. C. Harrold and L. E. Gordon, *J. Ind. Hyg. Toxicol., 21.* 491 (1939).

[30] F. A. Patty, *J. Ind. Toxicol., 21,* 469 (1939); *Industrial Hygiene and Toxicology,* Interscience, New York, 1948.

against mixtures of known concentration and of the same order as those in which the instrument is to be used; and (2) by calculation from the refractive index of the vapor and the experimentally established values of refractivity changes for an individual interferometer.[31]

Stamm suggested the use of the Lorentz-Lorenz equation as a means of calibration. This eliminates the need of large gas chambers for calibration.[32]

The interferometer method is only applicable to the quantitative determination of gases and vapors whose index of refraction differs sufficiently from that of air, since not all impurities produce a marked change in the refractive index of air. The instrument is nonspecific, and where several contaminants are present the reading obtained is due to the combined effects of all. Another disadvantage is that the interferometer is not adequate for estimating very low concentrations of gas and vapor; hence the instrument cannot be used advantageously for the evaluation of vapors of high toxicity. For example, the interferometer is not suitable for estimating concentrations of acrylonitrile in air below 90 parts per million. Since the maximum allowable concentration of the compound is 20 parts per million, it is clear that some method other than the interferometer must be employed.

b. Conductivity Methods

These methods when used for solvents containing carbon depend upon the combustion of carbon to carbon dioxide with the subsequent absorption of the carbon dioxide in some medium whose conductivity will be changed. The measurement of carbon dioxide conductometrically by the Thomas[33] method is based on the fact that the conductance of a carbonate solution is only half that of the hydroxide solution of the same concentration.

Carbon disulfide may be burned to sulfur dioxide, the sulfur dioxide is oxidized to sulfur trioxide, the sulfur trioxide is absorbed, and the change in conductivity noted.[34]

While hydrocarbons of a less poisonous nature, like gasoline, can be burned to yield sufficient carbon dioxide to give good results with the conductivity method, it fails for other substances like benzene, which cannot be detected in low enough concentrations.[35]

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[31] J. D. Edwards, *U. S. Bur. Standards, Tech. Paper 131* (1919).

[32] R. F. Stamm and W. R. Bradley, *Use and Calibration of the Interferometer in the Field of Industrial Hygiene*. Presented at Meeting Am. Ind. Hyg. Assoc., Metropolitan N. Y. Section, Jan. 1947.

[33] M. D. Thomas, *Ind. Eng. Chem., Anal. Ed., 5,* 193 (1933).

[34] M. D. Thomas, *Ind. Eng. Chem., Anal. Ed., 4,* 253 (1932).

c. Absorption of Radiant Energy

If light of a certain wave length is passed through air containing a vapor such as that of mercury or a solution containing some light-absorbing medium or substance, it will be absorbed. The fundamental law of the absorption of radiant energy is Beer's law, which states that the absorption of light depends upon the thickness of the layer traversed and on the molecular concentration of the absorbing medium in that layer. This is the basis of the photoelectric mercury detector developed by the General Electric Company for the detection of mercury vapor in air.[35,36] The degree of opaqueness to ultraviolet light with a wave length of 2,537 Å is a measure of the concentration of mercury vapor in air. The absorption is measured with a photoelectric cell.

Hanson[37] has devised an instrument using the principle analogous to the foregoing, namely that all vapors absorb light and therefore are partially opaque in some region of the spectrum.

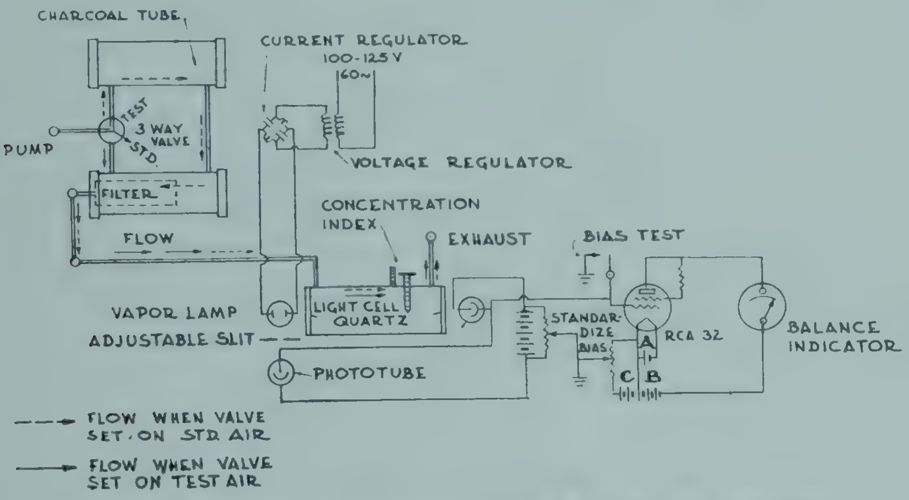
CHARCOAL TUBE
CURRENT REGULATOR
100-125 V
60~
TEST
3 WAY VALVE
STD
PUMP
VOLTAGE REGULATOR
FILTER
CONCENTRATION INDEX
FLOW
EXHAUST
BIAS TEST
VAPOR LAMP
LIGHT CELL QUARTZ
STANDARDIZE BIAS
A
RCA 32
BALANCE INDICATOR
ADJUSTABLE SLIT
PHOTOTUBE
C
B
FLOW WHEN VALVE SET ON STD AIR
FLOW WHEN VALVE SET ON TEST AIR

Fig. 104. Schematic arrangement of R. & H. Tri-Per-Analyzer.[7]

This instrument is shown diagramatically in Figure 104. It consists of a light cell 15 cm. long through which the sample is continuously pumped. A micrometer screw is inserted in the path of the light in front of the phototube. This is arbitrarily set at zero initially and the phototube circuit is adjusted to bring the microammeter "balance indicator" to mid-scale when solvent free air is in the cell. Such solvent free air is provided by pumping the sample through a charcoal tube, which removes the vapors in question from the sample. After the instrument is balanced, a three-way valve is turned to bypass the charcoal tube and to permit the solvent-laden air to pass directly into the cell. The solvent vapor in the air absorbs light in proportion to its concentration according to the Beer law, causing the "balance indicator" to shift to the left. The "balance indicator" is again brought back to mid-scale by turning the screw to reduce its shadow on the phototube. The concentration is then determined from a calibration curve provided with the instrument. The maximum sensitivity of the R & H Tri-Per Analyzer is given in Table 21. It does not respond to the vapors of the following solvents: methylene chloride, carbon tetrachloride, dichlorodifluoromethane, ethylene dichloride, tetrachloroethane, chloroform, methyl chloride, vinyl chloride, methyl alcohol, ethyl alcohol, amyl alcohol, ethyl acetate, ethyl Cellosolve, methyl Cellosolve, Dowtherm A, and water vapor. It is clear from Table 21 that this instrument is far more sensitive to mercury than any other substance. Hence, mercury is a serious interference.

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[35] P. Drinker, *Am. J. Pub. Health, 30,* 1063 (1940).

[36] Biggs, *J. Ind. Hyg. Toxicol., 20,* 161 (1938).

[37] V. F. Hanson, *Ind. Eng. Chem., Anal. Ed., 13,* 119 (1941).

TABLE 21

Maximum Sensitivity of R. & H. Tri-Per-Analyzer to Various Vapors[37]

Substance	Sensitivity, ppm./scale division	Substance	Sensitivity, ppm./scale division
Mercury	0.0001 (approx.)	Vinyl acetylene	2.0
Tetraethyl lead	0.13	Phosgene	5.0
Xylene	0.2	Acetone	5
Monochlorobenzene	0.3	Ethylbenzene	5
Aniline	0.3	Pentachloroethane	7
Perchloroethylene	0.5	Hydrogen sulfide	8
Toluene	1.0	Trichloroethylene	10
Chloroprene	1.0	Carbon disulfide	12
Diphenyl	1.0	*n*-Heptane	25
Benzene	1.2	Gasoline (Blue Sunoco)	50

Quartz Spectrophotometer. Andrews and Peterson[38] obtained the concentration of benzene and xylidine in experimental chambers by use of a quartz spectrophotometer. Evacuated Shepherd flasks and bulbs equipped with two stopcocks were used for sampling.

To dissolve the vapor introduce a carefully measured volume of isooctane, 2,2,4-trimethylpentane, through a small opening in the neck of the Shepherd flask or through a stopcock of the bulb with a hypodermic syringe and needle. Close the cap or stopcock, shake the flask gently, and allow to stand for several hours to assure equilibrium between vapor and solvent. With benzene cool the flasks in ice before withdrawing the sample for measurement.

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[38] H. L. Andrews and D. C. Peterson, *J. Ind. Hyg. Toxicol.*, *29*, 403 (1947).

Aternatively two all-glass midget impingers in series may be used for sampling. Place 10 ml. of isooctane in each impinger and draw the air to be sampled slowly through at a rate of 0.2 liter per minute. Restore any loss in volume of the solvent attributable to evaporation by the addition of solvent. One impinger is generally adequate.

Obtain the density of a 1-cm. length of benzene solution at 255 mμ with 1.6-μ slit width, and of xylidine solution at 289 mμ with 1.4-μ slit width. With benzene, 0.025 mg. per ml. could be detected and with xylidine, 0.004 mg. per ml.

d. Vapor Pressure[39]

In the vapor-pressure method a freezing agent is used to condense vapors from an atmosphere while it is passing through a trap, which is maintained at a temperature below the melting point of the material to be estimated. The system may then be evacuated, brought to room temperature, and the pressure developed by the revaporized compound measured with a manometer.

Couchman and Schultze[40] describe a method in which vapor-laden air is drawn through a specially designed trap (Fig. 105) immersed in a Dry Ice and acetone mixture, which freezes out the vapor. The trap is then evacuated while in the freezing mixture. The pressure of the compound in the vapor state is measured at room temperature in an attached mercury manometer.

Quantitative results may be obtained with vapors whose melting points are above —63° C., for amounts of vapor which are completely volatile at room temperature. For substances having lower melting points, liquid nitrogen may be used.

One variation of this method uses a glass coil of small volume in which the solvent from a large sample is frozen.[41] The pressure of the revaporized material is then noted.

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[39] G. A. Burrell and G. W. Jones, *U. S. Bur. Mines, Tech. Paper 87* (1916).

[40] C. E. Couchman and W. H. Schultze, *J. Ind. Hyg. Toxicol., 21*, 256 (1939)

[41] K. Kay, G. M. Reece, and P. Drinker, *J. Ind. Hyg. Toxicol., 21*, 264 (1939).

Another vapor-pressure instrument[42] consists of two identical 65-ml brass cells partially filled with bronze balls and provided with inlet and outlet valves. The instrument is connected to an inclinable manometer. Enough water to saturate that volume is placed in both cells and the instrument is immersed in a Dry Ice freezing mixture. The contaminated atmosphere is drawn through one cell and frozen out. All valves are then closed and the instrument is warmed in a water bath and shaken. It is then connected to the manometer and the pressure read. The second cell serves as a compensator and corrects for pressure changes attributable to temperature and water vapor.

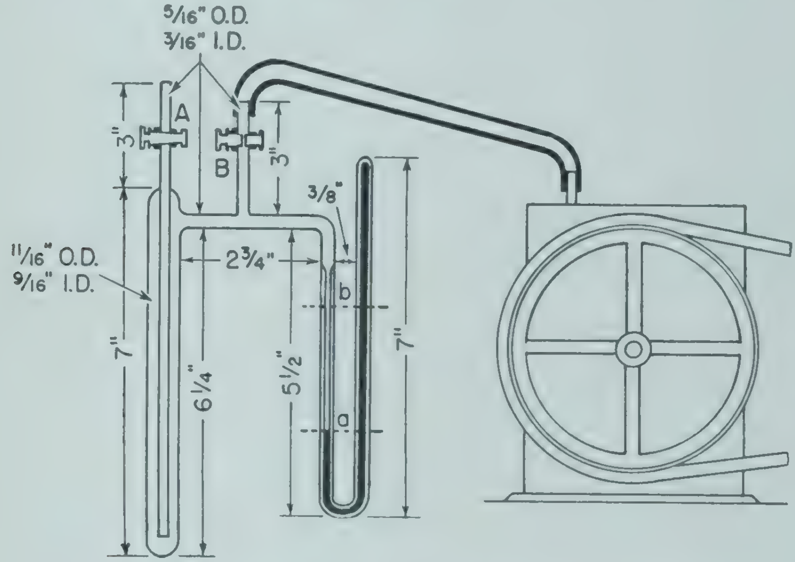

Fig. 105. Freezing trap, manometer, and vacuum pump.[40]

e. Specific Gravity

Devices have been developed which enable one to estimate the concentration of solvent vapors in air by the difference in specific gravity of pure air containing the solvent. Such instruments have found little employment because in many instances concentrations of the order of threshold limits scarcely produce a significant change in the specific gravity of the working room air.

One device called the Ranarex gas detector[43] is based on the laws of dynamics of gaseous bodies. The gas to be investigated is drawn into a round chamber in rapid rotation. In a second similar chamber, solvent-free air is introduced. If the specific gravities of the atmospheres of these chambers are different, there will be different moments of rotation which are proportional to the specific gravities of the gases. By adequate couplings connected to pointers and calibrated scales, the concentration of solvent vapors can be obtained by conservation.

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[42] L. Silverman, G. M. Reece, and P. Drinker, *J. Ind. Hyg. Toxicol.*, *21*, 270 (1939).

[43] Allegemeinen Elektrizitäts-Gesellschaft (AEG), Berlin.

f. Viscosity

It has been shown by Dommer[44–46] that vapors of solvents like benzene, benzine, ether, and others traverse a capillary faster than does air. Based on this principle, the concentration of vapor in an atmosphere can be obtained. Thus two capillaries of equal diameter can be attached to a manometer, to two orifices of equal diameter, and to the same source of suction. If the air to be tested is drawn through one of these capillaries and pure air is drawn through the other, there will be an increase in pressure on the test air side which is attributable to the more rapid flow and the fact that vapors of higher specific gravity than air will find a greater resistance to passage through an orifice. This difference in pressure may be read on the manometer and can be related to the concentration of the vapor in air. A device built on this principle is the "Union Gas Tester." About 0.02 per cent of benzine in air can be detected by this device.

g. Diffusion

If one has a device consisting of two chambers separated by a membrane permeable to a gas, through one chamber of which an atmosphere containing a gas heavier than air is flowing and through the other of which pure air is flowing, then air will diffuse from the pure air stream into the air–vapor stream causing a decrease in the pressure of the pure air chamber and an increase in pressure in the other chamber. If, however, the gas–air stream contains a gas lighter than air such as methane, the reverse process will occur.

This principle has been used for the construction of devices as vapor indicators.[47–49] By connecting the two chambers separated by the permeable membrane to a manometer, the difference in pressure can be

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[44] O. Dommer, U. S. Patent 1506617 (1924).

[45] O. Dommer, *Chem.-Ztg., 51,* 413 (1927).

[46] O. Dommer, *Arch. Wärmewirt., 8,* 92 (1927).

[47] A. Salmony-Karsten, *Gesundh.-Ing., 52,* 655 (1929).

[48] A. Sander, *Chem-Ztg., 56,* 390 (1932).

[49] G. Schmitt, *Brennstoff-Chem., 10,* 462 (1929).

noted and the amount of vapor calculated. The "Vulcan Gas Anzeiger" and the "Moment Gas Anzeiger, Glückauf" are variations of this device.

In another variation, a manometer is not used. The difference in pressure created by the diffusion is used to open or close an electric circuit in a rod-shaped detector, about 27 cm. long and 400 g. in weight, so that a small lamp operated by dry batteries glows. For instance, if this instrument is brought into an atmosphere containing illuminating (manufactured) gas, the diffusion produces an increase in pressure which closes the circuit and makes the lamp glow. In testing for gases heavier than air, the contact is set for lighting the lamp, the decrease in pressure resulting from the diffusion of the solvent vapor causes the circuit to break and the light goes out. This will also happen in an atmosphere which contains a gas heavier than air, like carbon dioxide.

h. Thermal Conductivity

The thermal conductivity of a gas is a measure of the quantity of heat conducted in unit time between two unit surfaces in the gas when they are unit distance apart and the temperature difference is 1° C. As Minter[50] point out, it is essential if the method is to be used, that the gases in a mixture possess thermal conductivities of sufficient difference in magnitude to produce a measurable difference in thermal conductivity for a small change in the composition of the mixture.

The quantity of heat conducted by a vapor or gas varies with the composition of the gas, ranging from poorly conducting vapors having only one-fifth the conductivity of air to hydrogen having seven times the conductivity of air.

One instrument is designed on the Wheatstone bridge principle.[50] It consists of two similar cells containing two similar current-heated filaments to two similar inert resistances. One cell contains air or the reference gas, the other contains a gas or vapor of different thermal conductivity. The heated filaments will be at different temperatures in these different atmospheres and the bridge will be unbalanced because of the different resistances of the filaments. The amount the bridge becomes unbalanced, which can be measured by a meter, will depend on the conductivity of the test atmosphere with respect to the reference atmosphere.

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[50] C. C. Minter, *J. Chem. Education*, *23*, 237 (1946).

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CHAPTER XIII

Paraffin and Unsaturated Aliphatic Hydrocarbons

The paraffin and unsaturated hydrocarbons of the aliphatic organic-chemical classification are assuming an ever-increasing importance in our present-day civilization. The use of both natural gas and manufactured gas such as coal gas, carburetted water gas, coke oven gas, and petroleum oil derivatives as fuels is increasing. Little need be said about the growing consumption of gasoline in internal-combustion engines of many types, for with traffic conditions as they are, that increase is self-evident. The use of acetylene for the manufacture of many synthetic materials has expanded and will grow greater. Within recent years the use of ethane, propane, and butane as refrigerants and fuels has been developed commercially. The use of liquid aliphatic hydrocarbons as solvents in dry-cleaning, extraction, and degreasing plants and as diluents in the paint and varnish industry has increased in large measure.

This increase in use of these substances, particularly the lower homologues, has produced another group of industrial hazards, which differ, however, from those we have previously encountered. As a group these substances are not industrial hazards because they are poisonous compounds but rather because the dangers in their use arise from two main sources. First, these substances may be present in sufficient quantity to reduce the oxygen content of air, below the level which is safe for human beings, in a confined space like a sewer or tank or even a relatively open space like a mine. This condition may be illustrated by the collection of methane in the places mentioned. Second, these substances form inflammable and explosive mixtures with air or oxygen and thus are fire and explosion hazards. A subsidiary danger is the possible production of carbon monoxide by the incomplete combustion of these substances.

The general fire hazard of ethane, propane, and butane—and methane may also be included—is in a class with that of casing-head gasoline, gasoline vapor, and illuminating gas[1,2]; that is , these substances rate from 90 to 100 in comparison with ether, which rates 100, in accordance with

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[1] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 1130* (1923).

[2] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

the Schedule of Classifications[3] of the Underwriters' Laboratories, Inc., as shown in Table 22.

TABLE 22

Fire-hazard Rating

Sustance	Rating
Ether	100
Gasoline	90–100
Ethyl alcohol	60–70
Kerosene	30–40
Paraffin oil	10–20

Methane and ethane are simple asphyxiants. Propane and butane have narcotic properties. The higher saturated hydrocarbons are narcotic, irritant, and convulsive.[4]

A. SATURATED ALIPHATIC HYDROCARBONS

1. Methane

a. Occurrence of Hazard

Methane, CH_4, or marsh gas, commonly called "firedamp" or "gas" by the miner, and known as light carburetted hydrogen in old books of chemistry and mine gases, is found in all coal mines, in some metal mines, among the gaseous products of explosions, in sewers, and sometimes in manholes, conduits, and like tunnels where pipe lines conveying manufactured gas are present. It is present even in coal mines deemed to be "nongassy" by miners, but probably only in small amounts in these instances. It derives its common name of marsh gas from the fact that the decomposing muck of stagnant ponds yields this gas when stirred. Its presence in all coal mines is due to the fact that methane escapes from coal through the spaces and pores of the coal and through the fissures and cracks of the coal vein. Methane, however, appears to be the only inflammable gas issuing from coal. The U. S. Bureau of Mines,[5] after having analyzed thousands of samples of gas from mines, states that it is very rare for any other inflammable gases to be found in a proportion of more than one- or two-hundreths of 1 per cent (0.01–0.02 per cent) of the mine air, unless by leakage of natural gas from a gas well which penetrates or passes near the coal mine. The presence of ethane is a good indication of such leakage. Crushed coal will, however, yield other inflammable hydrocarbons.

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[3] *Nat. Bd. Fire Underwriters*, "List of Inspected Gas, Oil and Miscellaneous Appliances," Dec., 1938.

[4] W. F. von Oettingen, *U. S. Pub. Health Service, Bull. 255* (1910)

[5] *Fed. Bd. Vocational Education, Bull. 39* (1931).

Methane is an important component of natural gas and of a number of manufactured gases. The chief poisonous property of these gases, as can be seen from Table 23, is due to the presence of carbon monoxide in the manufactured gases. Pure natural gas contains no carbon monoxide, therefore small gas leaks of natural gas do not cause poisoning from carbon monoxide, as is the case with manufactured gas. In recent years, however, during the season of heavy demand, some manufactured gas has been added to the natural gas distributed in Pittsburgh.[6]

TABLE 23

Composition of Natural and Manufactured Gases

Components	Natural gas[a]	Natural gas[b]	Coal or Coke-oven gas[a]	Oil gas[b]
Methane, CH_4	84.7	32.3	33.9	27.0
Ethane, C_2H_6	9.4	67.0	...	...
Propane, C_3H_8	3.0	...	...	...
Butane, C_4H_{10}	1.3	...	...	...
Ethylene, C_2H_4, and other illuminants	...	...	3.5	2.7
Carbon dioxide, CO_2	...	...	2.2	2.8
Carbon monoxide, CO	...	...	6.8	10.6
Oxygen, O_2	...	...	0.3	...
Hydrogen, H_2	...	...	47.3	53.5
Nitrogen, N_2	1.6	0.7	6.0	3.4

[a] A. C. Fieldner, *U. S. Bur. Mines, Inform. Circ. 6009* (1937).
[b] *Handbook of Chemistry and Physics* (21st ed.), Cleveland (1936–37).

b. Physical Properties

Methane is a colorless, odorless gas. It is about half as heavy as air, having a specific gravity of 0.555 referred to air as 1.0, at standard temperature and pressure, and its weight in grams per liter under the same conditions is 0.7168. It boils at −161.6° C. It has a critical temperature of −81.8° C. and a critical pressure of 54.9 atmospheres and therefore cannot be easily liquefied. It is a combustible gas and it is known that when mixtures of air and methane containing from 5 to 15 per cent of methane are ignited the flame produced will spread so rapidly that an explosion will result. These percentages are known as the lower and upper explosive limits of methane. Near the lower limit the explosion is not violent and can readily be followed with the eye. When about 9.5 per cent of methane is present in the mixture the explosion will be the most violent, for that mixture has just enough oxygen in it to burn all the methane, and the burning takes place almost instantaneously. Methane cannot be ignited without catalytic agents unless heated to about 700° C.

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[6] A. C. Fieldner, *U. S. Bur. Mines, Inform. Circ. 6009* (1937).

Methane is an odorless gas. However, because it is so often associated with stagnant air spaces in mines there is an accompanying "musty" odor, which some attribute to the methane. Where methane is contaminated with other gases which have odors, the odors of these other substances are often attributed to methane.

c. Toxicity and Physiological Response

Methane is not a poisonous gas. It belongs to that group of gases which in concentrations up to at least 20 per cent by volume do not appear to produce injury. If, however, the methane present in an atmosphere serves to reduce the amount of oxygen present drastically, there is the danger of asphyxiation.

Fieldner[6] tells the story of the miner who, in an examination for a fire-boss's certificate, answered the question of "Why is firedamp dangerous?" as follows: "Fire damp is composed of methane, which has the chemical formula CH_4. A mixture of methane and air on ignition undergoes the following violent reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. Should the unfortunate miner escape death by the violence of the explosion, or asphyxiation by the carbon dioxide, he would surely be drowned by the water formed."

Fieldner hastened to add that perhaps the miner being examined overestimated the water hazard; nevertheless, the products of combustion are a real hazard not so much because of the carbon dioxide, which is the product of complete combustion, but rather because of the carbon monoxide formed by incomplete combustion.

d. Methods of Detection

Methane is only slightly soluble in water and is not readily absorbed by absorbing solutions. In gross gas analysis, methane is treated similarly to hydrogen. That is the other gases of the component mixture are absorbed and the methane is finally burned to carbon dioxide. It is then estimated as carbon dioxide. Because of the slight reactivity of methane, other methods of detection must be used for relatively small concentrations. These fall into two main groups: (1) flame safety-lamp detectors and (2) electrical detectors.

Flame Safety-Lamp Detectors. There is no record as to who first discovered that a flame becomes elongated in the presence of methane, nor is there any record as to when this discovery was made. There is little doubt that the candle flame was the earliest of the many schemes that were devised for methane detecting. The use of the candle was probably responsible for as many explosions and deaths as for the number of lives it saved. About 1816, the Davy flame safety lamp was introduced into coal mines. Its flame could be used in much the same manner as the candle to indicate the amount of methane present in the mine atmosphere. This device can be considered as the first safety methane detector.[7]

For the history of the development of methane-detecting devices, the reader is referred to Ilsley and Hooker.[7]

In the United States the principal permissible flame safety lamps are various models of the Koehler and Wolf flame safety lamps. The construction and use of these lamps and also of some foreign types are completely discussed and described by Forbes and Grove.[8] The flame safety lamp has decidedly definite limitations as a gas detector. It is doubtful whether the average observer can detect less than 1 per cent of methane with the ordinary lamp or less than 0.5 per cent with the improved lamp. When there is sufficient methane present to be detected with a flame safety lamp, the amount may be roughly estimated by the height of the "cap," or elongation of the flame, but these estimates are likely to differ considerably from the true value. While the flame safety lamp is of value in mines and in tunnels, that is, in places which have simple modes of entrance and exit, they are of little practical value for use in confined spaces and some other method of detection must be used.

Behavior of Flame. When atmospheric conditions are normal the flame of a safety lamp has a normal flame appearance, but when the atmosphere undergoes certain changes the appearance of the flame is altered, and it is these differences in the flame that make the safety lamp of value for testing mine air.

If the oxygen of the atmosphere becomes lower than normal, the flame of the lamp grows dim, and when the oxygen gets as low as about 16.25 per cent, the flame is extinguished. If the normal flame of the lamp is placed in an atmosphere that contains combustible or inflammable gas, some of the gas inside the lamp nearest the flame will burn and will increase the length of the lamp flame. The elongation of the flame of a safety lamp caused by methane or other inflammable gas is called the gas "cap" and the height of this cap may be used to indicate the amount of gas present in the air that surrounds the lamp. A safety-lamp flame will show the presence of gas before the percentage of gas reaches the lower explosive limit.

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[7] L. C. Ilsley and A. B. Hooker, *U. S. Bur. Mines, Inform. Circ. 6733* (1933).

[8] J. J. Forbes and G. W. Grove, *U. S. Bur. Mines. Miners' Circ. 33* (1938).

The elongation of the flame caused by methane is a pale-blue flame cap that appears to ride on or cover the lamp flame. Two different methods are employed for testing for methane with an ordinary service lamp: (1) use of a short, almost nonluminous flame, and (2) use of a normal service flame about 1 inch high. The short flame is better suited for accuracy and probably also better from the standpoint of safety.

The effect of oxygen deficiency on methane detection is pronounced. A reduction of oxygen below normal (20.94 per cent of oxygen in air by volume) will materially affect the efficiency of methane testing with a flame safety lamp because the lower oxygen concentration rapidly affects the illuminating power and consequently the heat of the flame. The relationship between the illuminating power of a flame safety lamp and the oxygen concentration is as follows:

Per cent oxygen	Per cent illumination
20.93	100
20.70	90
20.30	75
19.90	70
19.30	40
18.90	28
18.30	12

In view of the rapid decrease of illumination with a small reduction of oxygen content, it is clear that the flame safety lamp will not be an efficient device for detecting methane in any atmosphere with an appreciable oxygen deficiency. Its limit of applicability is considered to be an atmosphere containing at least 19 per cent of oxygen.[8]

Electrical Detectors. The electrical detectors for the detection and estimation of methane may be classified into three groups: (1) the combustion type, represented by the Burrell[8-11] methane detector and the Jones[12] gas detector; (2) the catalytic type, represented by the U. C. C. detector[13] and the M. S. A. detector; and (3) the diffusion type, represented by the Neufeldt and Kuhnke (German) methane detector and the Ringrose[14] (English) methane detector.

A rather complete description and discussion of various models of electrical methane detectors is given by Forbes and Grove. A fairly

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[9] G. A. Burrell, *Ind. Eng. Chem., 8,* 365 (1916).

[10] L. H. Milligan, *U. S. Bur. Mines, Tech. Paper 357* (1925).

[11] G. W. Jones and W. P. Yant, *U. S. Bur. Mines, Tech. Paper 352* (1942).

[12] Mine Safety Appliances Co., Pittsburgh, Pa.

[13] Union Carbide and Carbon Chemicals Corp., New York. N. Y.

[14] L. C. Ilsley and A. B. Hooker, *U. S. Bur. Mines, Circ. 6733* (1933).

complete listing is given by Ilsley and Hooker. All of the electrical devices except the Jones gas detector have the disadvantage that they cannot operate efficiently in atmospheres of oxygen deficiency, that is, more than 16 per cent of oxygen must be present in the sample tested.

Combustion-type Burrell Detector. In 1915 the Burrell methane detector was developed by G. A. Burrell of the U. S. Bureau of Mines. It is a simple device that will quickly and with reasonable accuracy determine small quantities of methane in mine air. However, it can be used to estimate methane present in other places and has been adapted to the analysis of mixtures of air with any other combustible gas or vapor, such as hydrogen or gasoline vapor, which is virtually insoluble in water, and of which the average composition is known. This detector is really a special type of gas-analysis apparatus for determining the percentage of methane in air by slow combustion. It uses a platinum-wire glower at bright-yellow heat to burn the gas. Methane burns according to the following reaction:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

That is, 1 volume of methane plus 2 volumes of oxygen yields 1 volume of carbon dioxide and 2 volumes of water. The water vapor condenses at ordinary temperature to liquid water, which occupies a negligible volume. Hence the volume of methane can be calculated from the difference between the volume of the sample drawn into the detector and that of the residual gas after burning. This is a contraction and is twice the volume of the methane originally present.

The detector is essentially a water-filled U-tube, one end of which ends in a combustion chamber containing the glower and the other end in a gauge glass having a calibrated scale.

Procedure. To make the test, water is forced into the combustion chamber and also into the valve cup by blowing into a rubber tube connected to the calibrated arm of the U. When the water is allowed to return to the original position, it draws a measured sample of the air to be tested through the valve into the combustion chamber. The level of water always returns to the same mark on the gauge glass and therefore draws in a known volume of sample (31 ml.). The valve is closed and the methane is burned by closing a switch and electrically heating the platinum wire. The contraction in volume after burning is shown by the new position of the water level in the gauge glass adjacent to the calibrated scale, which indicates the percentage of methane present in the sample. The scale of the detector was not calculated directly from a contraction basis but was made to include such factors as the solubility of methane in water prior to burning and that of the carbon dioxide formed after burning.

The Burrell detector gives relatively accurate determinations of methane percentage when analyzing air containing less than 4 per cent of methane by volume. Mixtures containing gas up to the higher explosive limit (15 per cent) are readily recognizable because they explode inside the instrument. It will not work with proper efficiency if used in an atmosphere containing less than 16 per cent of oxygen

The Jones combustible-gas indicator and the catalytic types of electrical indicators are briefly described in Chapter XII (pages 478–482).

e. Determination

Because, as was mentioned previously, methane is only slightly chemically reactive, practically insoluble in water, and only moderately soluble in ethyl alcohol and in other common solvents, it cannot be trapped by absorption or adsorption. Because of its low boiling point, (—161° C.), its low critical temperature (—81.8° C.), and its high critical pressure (54.9 atmospheres), it cannot be simply trapped by freezing or by condensation. Furthermore, because it is not poisonous, very small quantities of methane in air are a negligible industrial hazard. It should, however, be noted that while a mixture of air and methane is not explosive until 5 per cent of methane is present, which is relatively a high percentage of this gas, experiments have shown that the presence of less than this amount of methane in mine air greatly increases the chance of dust explosions, so that even 1 or 2 per cent of methane in a dusty atmosphere may be an explosive mixture and thus a fire hazard.

For the determination of amounts of methane under most conditions where it might be an industrial hazard, it is best to take a grab sample by means of vacuum displacement or by one of the other appropriate methods detailed in Chapter II.

The absorbable gases of this sample are then absorbed in an appropriate absorbent; for instance, in the Orsat method, carbon dioxide is absorbed by sodium or potassium hydroxide, oxygen is absorbed by alkaline pyrogallate, carbon monoxide is absorbed by cuprous chloride, then the methane is burned in an excess of oxygen, and the amount present is estimated by the reabsorption of the carbon dioxide produced by the combustion. The difference in volume, measured by a gas burette, before and after absorption of a component of the gas mixture in an absorbent will be a measure of the volume of that gaseous component present. In the Haldane[15,16] method, the carbon dioxide of the gas sample is removed by passing the gas from the burette to which it had been transferred into a pipette that contains an alkaline medium. Combustible gases like

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[15] J. S. Haldane and J. I. Graham, *Methods of Air Analysis*, Griffin, London, 1935.
[16] L. B. Berger and H. H. Schrenk, *U. S. Bur. Mines, Inform. Circ. 7017* (1938).

methane are determined by passing the gas sample into a pipette containing an electrically heated platinum wire that causes these gases to burn. Carbon dioxide produced by this combustion is removed again by passing the gas into a pipette that contains potassium hydroxide solution.

When hydrocarbon gases are burned in the presence of an excess of oxygen there is a loss of volume, and for each gas mixture the contraction in volume is proportional to the quantity of that gas originally present. As was explained on page 503, methane completely burned yields carbon dioxide and water vapor, and as the water vapor condenses to liquid water, the contraction in volume is two, for three volumes of the reacting gases were originally present and after the condensation of two volumes of water vapor only one volume of carbon dioxide remains. For each hydrocarbon gas present, the amount of contraction is directly proportional to the amount of that gas.[17] Table 24 gives the combustion data of the hydrocarbon gases and vapors.

For the details of gas analysis the reader is referred to the texts listed at the end of the chapter, to Yant and Berger,[17a] and to Berger and Schrenk.[16]

An alternative and less widely used combustion method is one in which gases capable of yielding carbon dioxide are removed by passage through sulfuric acid, soda lime, silica gel, and a freezing mixture. The resultant gas is passed over a platinum spiral at red heat and the carbon dioxide produced is absorbed in a known volume of standard barium hydroxide. The excess barium hydroxide solution is titrated with standard hydrochloric acid solution. One ml. of 0.02 *N* hydrochloric acid solution is equivalent to 0.16 mg. of methane.

Methane and ethane are completely oxidized by excess oxygen when passed over a platinized silica gel catalyst at 610° C.[18] Higher hydrocarbons are also oxidized at this temperature. Absorb all components of a gas mixture including carbon monoxide; determine hydrogen by oxidation at 100° C.; and raise the temperature of the catalyst tube to 610° C. for the hydrocarbon estimation.

2. *Ethane, Propane, and Butane*

Ethane, propane, and butane are hydrocarbon gaseous homologues of methane. In recent years their use has been commercially developed in two main fields, refrigeration and fuels. For example, ethane is used in

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[17] G. W. Jones and W. P. Yant, *U. S. Bur. Mines, Tech. Paper 352* (1924).

[17a] W. P. Yant and L. B. Berger, *U. S. Bur. Mines, Miners' Circ. 34* (1936).

[18] K. A. Kobe and W. I. Barnet, *Ind. Eng. Chem., Anal. Ed., 10,* 139 (1938).

TABLE 24

Combustion Data of the Hydrocarbon Gases Existing in Petroleum Vapors[17]

Hydrocarbons	Formula	Molecular weight	Chemical reaction when burned with oxygen (air)	Volume required for complete combustion		Products of combustion per volume of gas burned			Contraction produced when volume of gas is burned	Lower flammable limit	Contraction produced when 100 ml. of vapor-air mixture at lower flammable limit is burned	Max. allowable concn.
				O_2	Air	CO_2	H_2O vapor	N_2				
Methane	CH_4	16.03	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	2.0	9.50	1.0	2.0	7.56	2.0	5.50[a]	....	....
Ethane	C_2H_6	30.05	$C_2H_6 + 3^1/_2O_2 \rightarrow 2CO_2 + 3H_2O$	3.5	16.72	2.0	3.0	13.23	2.5	3.10[b]	7.75	....
Propane	C_3H_8	44.06	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	5.0	23.89	3.0	4.0	18.90	3.0	2.15[b]	6.65	....
Butane	C_4H_{10}	58.08	$C_4H_{10} + 6^1/_2O_2 \rightarrow 4CO_2 + 5H_2O$	6.5	31.06	4.0	5.0	24.57	3.5	1.65[b]	5.80	....
Pentane	C_5H_{12}	72.10	$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$	8.0	38.22	5.0	6.0	30.24	4.0	(1.35)[c]	5.40	1000
Hexane	C_6H_{14}	86.11	$C_6H_{14} + 8^1/_2O_2 \rightarrow 6CO_2 + 7H_2O$	9.5	45.39	6.0	7.0	35.91	4.5	(1.15)[c]	5.10	500
Heptane	C_7H_{16}	100.13	$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$	11.0	52.56	7.0	8.0	41.58	5.0	(1.00)[c]	4.90	500
Octane	C_8H_{18}	114.14	$C_8H_{18} + 12^1/_2O_2 \rightarrow 8CO_2 + 9H_2O$	12.5	59.72	8.0	9.0	47.25	5.5	(0.85)[c]	4.75	500

[a] G. A. Burrell and C. G. Oberfell, *U. S. Bur. Mines, Tech. Paper 109* (1915).
[b] M. J. Burgess and R. V. Wheeler, *J. Chem.*, *99*, 2013 (1911).
[c] Calculated.

refrigerating systems designed to give very low temperatures. Propane is also used in refrigerating systems which require low temperatures, while butane is used in domestic-type refrigerators.

Ethane is used as a fuel for lighter-than-air craft because this gas has practically the same density as air and does not alter appreciably the weight of the airship as it is consumed. Propane is used for domestic heating purposes.

Ethane, propane, and butane are components of natural gas and consequently are found in atmospheres where there are natural-gas leaks. Crude oils give off vapors in which these gases are present.

Propane is used in case-hardening and butane is used as a low-boiling extracting solvent.

a. Physical Properties

Ethane is a colorless, odorless, combustible gas which boils at —88.3° C. It has a specific gravity of 1.05 referred to standard conditions of temperature and pressure. It weighs 1.3565 g. per liter under the same conditions. It has a lower explosive limit of 3.3 and an upper explosive limit of 10.6, yielding an explosive range of approximately 7. At 20° C. about 4.7 ml. is soluble in 100 parts of water, but it is much more soluble in alcohol.

Propane is a colorless gas which has a characteristic natural-gas odor and which boils at —44° C. It is heavier than air and has a density of 1.56 referred to air at standard conditions of temperature and pressure. It weighs 2.02 g. per liter under the same conditions. It has a lower explosive limit of 2.4 and an upper explosive limit of 9.5, giving an explosive range of 7.1. At 17.8° C., 6.5 ml. is soluble in 100 parts of water, but it is over 100 times as soluble in alcohol at the same temperature.

Butane is a colorless gas of a characteristic natural-gas odor which boils at —0.3° C. It has a density referred to air of 2.01 and weighs 2.59 g. per liter under standard conditions. It has a lower explosive limit of 1.8 and an upper explosive limit of 8.4, giving an explosive range of 6.6. About 15 ml. is soluble in 100 parts of water at 17° C.

b. Toxicity and Physiological Response

Ethane, propane, and butane are not poisonous gases. They are anesthetic in action. They belong to that group of gases and vapors which do not appear to produce injury in concentrations up to 5 per cent by volume for durations of exposure of 2 hours.[19] White rats subjected to an atmosphere containing 6.3 per cent by volume of propane, without a deficiency of oxygen, become slightly drowsy. An atmosphere containing 37.5–51.7 per cent of propane inhaled for 2 hours by the rats produced muscular weakness and mild anesthesia.

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[19] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

c. Detection and Determination[19a]

Ethane, propane, and butane are only slightly reactive substances, very similar to methane in their chemical activity. They are not readily absorbed or dissolved in common absorbents although butane may possibly be separated by freezing. The principal method of analysis of gaseous mixtures containing several paraffin hydrocarbons is to liquefy the total gas and obtain separation of the different hydrocarbons by fractional distillation at low temperatures in a partial vacuum. Then each fraction is submitted to subsequent analysis by combustion methods.

The essential parts of the apparatus used for fractional distillation are a burette for measuring the sample, a liquefaction bulb, a mercury air pump for exhausting the liquefaction bulb, and a burette for collecting the distillates. The temperature of the liquefaction bulb is controlled by low-temperature baths contained in Dewar flasks. The temperatures of fractionation are: permanent gases and methane, —183° C.; ethane, —150 to — 145° C.; propane, —145 to —118° C.; butane and heavier hydrocarbons, —118 to 20° C.

Where it is known that a particular hydrocarbon gas or vapor is present in an atmosphere, say ethane, it may be detected and estimated as described in the procedures given for methane. The amount of ethane or other combustible hydrocarbon or vapor can be calculated from the contraction produced or the carbon dioxide evolved as given in Table 24.

With respect to their character as industrial hazards, the amount of each of these gases and vapors as components of a gaseous mixture is generally immaterial. What is pertinent is whether the mixture is explosive, how close to the explosive limit a particular atmosphere is, or whether an asphyxiating or toxic atmosphere is present. This will be obtained as readily by estimating total combustible gases present as by trying to determine the amount of the individual gases present, a procedure which the ordinary laboratory is not equipped to perform.

In general, then, ethane, propane, and butane are detected and estimated by the same methods used for methane, with scales on the instruments adjusted for combustible gases instead of methane.

[19a] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 1130* (1923)

3. Gasoline and Petroleum Vapors

Gasoline is most widely used because it has been found most satisfactory as a fuel for internal-combustion engines, especially those used in automobiles and trucks. It is, however, also widely used in lamps, irons, washing machines, stoves, and radiators as the fuel for which the machine was designed. Gasoline is also used as a cleaning solvent.

a. Physical Properties

Gasoline is obtained from crude petroleum oil, which is the source of a number of commercial products, including, in order of their volatility, petroleum ether, naphtha, benzine, kerosene, fuel oil, lubricating oil, and asphalt. *Petroleum ether* and *petroleum benzine* are the names used for the hydrocarbon fractions which boil in the range from 20–90° C. Petroleum ether generally used to designate the fraction boiling from 20–60° C., petroleum benzine a higher boiling fraction, from 40–90° C. *Naphtha* designates a still higher boiling fraction, from 65–120° C., and *benzine* an even higher boiling fraction, from 110–150° C. Gasoline covers the entire range, with at least 10 per cent boiling below 65° C. and at least 90 per cent boiling below 200° C. Casing-head, or natural, gasoline is obtained from certain gas wells by compressing and cooling the gas. This product is richer than ordinary gasoline in the volatile components and is not suited for the gasoline engine unless it is blended.

Gasoline is a mixture of paraffin hydrocarbons higher than butane, particularly pentane, hexane, heptane, and octane. These hydrocarbon vapors are similar to their lower homologues in their reactivity.

It is necessary to point out that gasoline and motor fuel are not synonymous. Motor fuel is an even more complex mixture than gasoline, for it contains additives like tetraethyl lead, xylidine, catechol, ethylbenzene, and other materials.

Because of the very low lower limit of explosibility of gasoline in air (1.4), only a very small amount of this material in a gaseous mixture is necessary to form an inflammable and explosive mixture. Air merely flowing over liquid gasoline and many crude oils readily become charged with enough hydrocarbon vapor to transmit flame on reaching some source of ignition such as a flame, an electrical spark, or a short circuit. A current of this vapor-laden air can transmit flame several hundred feet from the source of ignition.

The predominating hydrocarbons liberated by petroleum and its products from storage tanks, tankers, and similar places are butane and propane with the range from ethane to duodecane, $C_{12}H_{26}$.

b. Toxicity and Physiological Response

With the exception of high-sulfur petroleum and leaded gasolines, petroleum vapors are not very poisonous. Some crude oils, especially some of the Mexican crudes refined in the United States, give off a rather high percentage of hydrogen sulfide especially during distillation. The great toxicity of hydrogen sulfide has been discussed in Chapter IX (page 319). The toxicity of tetraethyl lead has also been described on page 220 and that of xylidine-blended gasoline on page 716.

Individuals vary greatly in their susceptibility to petroleum vapors not containing other poisonous components. About 0.3 per cent of gasoline vapor in air is required to make a man somewhat dizzy in 15 minutes. A man accustomed to breathing the vapors can endure larger percentages but 1 to 2.0 per cent of gasoline vapor will make most men dizzy in 3 to 5 minutes, and this percentage will endanger life if continued to be breathed for 1 hour or more.[20]

Guinea pigs exposed to an atmosphere containing $2^1/_2$ per cent by volume of gasoline for durations of exposure of 2 hours had violent convulsions.[20a]

Percentages of gasoline vapor in air sufficiently high to reduce the oxygen content below that needed for respiration will act as an asphyxiant. The recommended maximum allowable concentration for daily 8-hour exposures for gasoline, hexane, heptane, and octane is 500 parts per million parts of air by volume. That of pentane is 1,000 parts per million. The greatest hazard from gasoline and its vapors is due to its inflammability and explosibility.

c. Detection and Determination

Gasoline and petroleum vapors are detected through their property of inflammability. Because gasoline is a mixture of hydrocarbons and not a definite chemical compound, there can be no specific reaction for its estimation.

The instruments and devices described and discussed under methane can, in general, be used for the detection of an atmosphere made combustible by the presence of these vapors. They burn in an excess of oxygen to yield carbon dioxide and a contraction in volume. This con-

[20] A. C. Fieldner, *U. S. Bur. Mines, Inform. Circ. 6009* (1937).

[20a] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933)

traction in volume ranges from 4.75 ml. for octane to 7.75 ml. for ethane, when 100 ml. of vapor-air mixture at the lower flammable limit is burned (see Table 24).

The Burrell methane indicator has been adapted for the detection of petroleum vapors. On the principle that the only scale which would safely indicate an explosive mixture of petroleum vapor of unknown composition in air is one based on the gas or vapor which produces an explosive mixture with the least contraction, Jones and Yant[21] selected heptane. This selection made the Burrell indicator safe for all conditions of use. The instrument is used in a manner analogous to the method described for methane except that 0.3 per cent of petroleum vapor is considered the safety limit for the use of the instrument. This corresponds to about 1 per cent on the methane scale. For complete details see the reference.

Gasoline and petroleum vapors may also be adsorbed on activated charcoal or on silica gel, or they may be condensed by freezing. They may subsequently be liberated by distillation, burned to carbon dioxide in standard gas-analysis equipment, and estimated volumetrically, or catalytically oxidized to carbon dioxide, which is in turn estimated by one of the methods detailed for this gas in Chapter XI (page 442).

Methods for the determination of chemical hazards in the petroleum industry have been discussed by Jacobs.[21a]

4. Naphtha and Benzine

Naphtha and benzine are liquid aliphatic hydrocarbon derivatives of crude petroleum oil. They contain, however, more of the higher boiling homologues. These mixtures are widely used as fuels and as solvents, especially in the manufacture of rubber products, in degreasing plants, and as diluents in the paint and varnish industry.

a. Toxicity and Physiological Response

They are much more noxious than their lower boiling homologues. They cause headache and vertigo, nausea and vomiting, irregular respiration, drowsiness, irritation of skin and mucous membranes, and even mild intoxication. Lehmann and Hesse describe the following physiological response for these vapors. Concentrations of 30 to 40 mg. per liter or greater for 15 minutes to 1 hour cause death. Concentrations of 25 to 30 mg. per liter for 30 minutes to 1 hour are dangerous, while concentrations of 10 to 20 mg. per liter can be tolerated without immediate danger. Prolonged exposure to 5 to 10 mg. per liter will cause some of the symptoms mentioned above.[22]

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[21] G. W. Jones and W. P. Yant, *U. S. Bur. Mines, Tech. Paper 352* (1924).

[21a] Morris B. Jacobs, Am. Chem. Soc. Meeting, March, 1949.

Different grades of naphtha and benzine have varied physiological effects. Those grades containing relatively high amounts of unsaturated hydrocarbons are decidedly more irritating. Thus the maximum allowable concentration of petroleum naphtha is set at 500 parts per million while that of coal-tar naphtha is 200 parts per million.

b. Detection and Determination

Benzine and naphtha are detected and estimated by the methods indicated for gasoline. As in the instance of gasoline, because benzine and naphtha are mixtures of hydrocarbons and not definite chemical compounds no specific reactions can be used for their estimation.

The vapors of naphtha and benzine can be adsorbed on activated charcoal and silica gel, or they can be frozen out by the use of solid carbon dioxide or some equivalent freezing mixture, and weighed. The vapors can also be distilled and estimated volumetrically or can be burned, converted to carbon dioxide, and estimated as combustible vapors.

An alternative method is to trap the vapors in a weighed series of bubblers containing mineral oil. The mineral oil is first dried at 100° C. in a constant-temperature oven until there is a negligible loss in weight in order to free it of any volatile material. Then a measured volume of the atmosphere to be tested, previously dried and freed from carbon dioxide by the usual methods, is passed through the weighed series of traps containing the mineral oil while it is surrounded by a dry freezing mixture. After approximately 1.5 cubic feet (45 liters) in about 3 hours has been drawn through the bubblers, they are removed, allowed to come to room temperature, and weighed. The increase in weight, divided by the volume of air sampled, gives the weight per unit volume according to the units of weight and volume used.

B. OLEFINIC HYDROCARBONS

1. *Ethylene and Gaseous Olefins*

Ethylene and some of its homologues are used in manufactured and natural gases to give them illuminating power. For this reason they are termed "illuminants." In recent years ethylene has been extensively used in the coloring of citrus fruits, tomatoes, bananas, and melons and in the blanching of celery, endive, and other vegetables, because it has the property of accelerating the mature coloring of fruits and vegetables. It is also used as a welding fuel and in its pure state as an anesthetic.

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[22] F. Flury and F. Zernik, *Schaedliche Gase*, Springer, Berlin 1931.

a. Physical Properties

Ethylene, C_2H_4, is a colorless gas of faint, pleasant, sweetish odor. It boils at —104.0° C. and can be condensed to a liquid at 10° C. and 50 atmospheres pressure. It has practically the same density as air, namely 0.97, and weighs 1.26 g. per liter at standard conditions. Because of the similarity of its density to that of air it diffuses readily. It is not very soluble in water but 1 volume of alcohol will dissolve $3^1/_2$ volumes of the gas. Ethylene is a combustible gas which forms explosive mixtures with air. It has a lower explosive limit of 2.7 and an upper explosive limit of 28.6, with a range of 25.9.

b. Toxicity and Physiological Response

Ethylene is not a poisonous gas. It acts as an anesthetic when inhaled in sufficient quantity and can be an asphyxiant. The greatest hazard from the use of ethylene is the danger from explosion and that it may reduce the oxygen content of an enclosed air space to such a point as to render it an asphyxiating atmosphere.

c. Detection and Determination

Ethylene is an unsaturated hydrocarbon and is consequently far more reactive than the saturated hydrocarbons discussed in the prior sections of this chapter. Thus it reacts readily with bromine, chlorine, hypochlorous acid, hypobromous acid, potassium permanganate, and concentrated sulfuric acid. Its ability to react with these substances is the basis for some of the methods for its estimation.

Because of its explosibility its presence in an atmosphere can be shown by the devices mentioned for methane.

Ethylene and its homologues are estimated volumetrically with standard gas-volumetric equipment by the contraction in volume noted with a gas burette before and after passing the sample being tested through fuming sulfuric acid in a gas pipette.

Olefins can be estimated volumetrically in the presence of one another by the method of Dobryanski.[23] He recommends 63 to 64 per cent sulfuric acid for absorbing isobutylene; 83 to 84 per cent acid for propylene, butadiene, and *n*-butenes; and 100 to 102 per cent acid for ethylene. Isobutylene is absorbed about 500 times as readily as propylene in 63 to 64 per cent acid and propylene is absorbed about 500 times as readily as ethylene in 83 to 84 per cent acid. Contact of a gas sample successively with acid of those strengths thus removes in turn isobutylene, propylene, and ethylene.

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[23] A. F. Dobryanski, *Neftyanoe Khoz., 9,* 565 (1925); *Petroleum Domain, 1925,* 565.

Matuszak[24] finds that for the determination of gaseous olefins to within 0.2 per cent, the absorbents listed in the following table are satisfactory.

TABLE 25

Absorbents for the Determination of Gaseous Olefins

Olefins	Preliminary absorbent	Final absorbent
Isobutylene	60–62% H_2SO_4	68–70% H_2SO_4
n-Butenes, propylene	80–82% H_2SO_4	88–90% H_2SO_4
Ethylene	88–90% H_2SO_4 + 0.9–1.0% Ag_2SO_4	98–100% H_2SO_4 + 0.4–0.5% Ag_2SO_4

The higher figure given in each range is considered to be the maximum permissible value. Intermediate and lower concentrations can be used. For example, concentrated sulfuric acid containing up to 0.7 per cent silver sulfate can be used as a final absorbent for ethylene.

2. *Butadiene*

Butadiene, $CH_2{:}CHCH{:}CH_2$, 1,3-butadiene, divinyl, diethylene, is a colorless gas at room temperature which has had extensive use as a raw material in the synthetic-rubber industry. It boils at —4.7° C.

Butadiene has a narcotic effect at high concentrations but otherwise appears to be innocuous.[24a] The recommended maximum allowable concentration is 1,000 parts of 1,3-butadiene per million parts of air by volume.

Determination

The concentration of 1,3-butadiene in air can be estimated by a variation of the iodine pentoxide method for ether (see pages 424 and 645). This reagent completely oxidizes butadiene, liberating 2.2 mols of iodine per mol of 1,3-butadiene.

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[24] M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed., 10*, 354 (1938).

[24a] C. P. Carpenter, C. B. Shaffer, C. S. Weil, and H. F. Smyth, Jr., *J. Ind. Hyg. Toxicol., 26*, 69 (1944).

Sample butadiene-air mixtures by use of gas burettes or gas-sampling tubes and displace by means of mercury through a tube containing iodine pentoxide at a temperature of 200° C. Collect the liberated iodine and titrate with standard sodium thiosulfate solution.

C. ACETYLENIC HYDROCARBONS

Acetylene

Acetylene is an unsaturated hydrocarbon gas widely used as a fuel for welding and for the production of high-temperature flames. It is also used as an illuminant. Its use in industry is expanding rapidly, for it is the starting material for the manufacture of acetaldehyde and of many synthetic chemicals and materials.

Acetylene, C_2H_2, is a colorless gas of characteristic garlic-like odor. It boils at —84° C.; weighs 1.17 g. per liter; and has a density of 0.91, referred to air at standard temperature and pressure. It is only slightly soluble in water, moderately soluble in alcohol, but very soluble in acetone, which solvent will dissolve 300 volumes of acetylene in 1 volume at 12 atmospheres pressure. It is explosive when compressed to 2 or more atmospheres but is safe when compressed and dissolved in acetone. It forms explosive mixtures with air, having a lower explosive limit of 2.5 and an upper limit of 80. This gives acetylene an explosive range of 77.5, which is one of the widest known, being greater than that of carbon monoxide or hydrogen. This wide range, of course, increases the explosion hazard of this substance. Thus, for instance, it is a special hazard in the production of liquid oxygen.

a. Toxicity and Physiological Response

Acetylene is a simple asphyxiant and anesthetic. It is moderately poisonous, thus a concentration of about 100 mg. per liter may be tolerated for $^1/_2$ to 1 hour. However, in the generation of acetylene from calcium carbide and water some dangerous impurities such as arsine and phosphine may be formed and thus make the contaminated acetylene a very toxic substance.

b. Detection and Estimation

Acetylene is an even more unsaturated hydrocarbon than ethylene. It reacts in a manner analogous to that of ethylene. It will react with chlorine, bromine, potassium permanganate, and hydrogen chloride. It forms, with an ammoniacal cuprous chloride or silver salt solution, a dark-red precipitate of cuprous or silver acetylide, which when dry is explosive.

Ilosvay Test.[25,26] *Reagent.* Place 1 g. of cupric nitrate, $Cu(NO_3)_2 \cdot 5H_2O$, or the chloride or sulfate salt in a 50-ml. volumetric flask and dissolve in water. Add 4 ml. of concentrated ammonium hydroxide solution and 3 g. of hydroxylamine hydrochloride, $NH_2OH.HCl$. Shake until the mixture is colorless and make to volume. The reagent will last longer if made with the nitrate salt. If the reagent is covered with mineral oil, or if copper wire is added, it will retain its reactivity for a longer period.

Procedure. Place 20 ml. of the Ilosvay reagent in a 500-ml. to 3-liter glass-stoppered cylinder or separatory funnel and pass in a measured volume of the gas to be tested or until the color of the reagent is pink. Stopper the cylinder or funnel and shake frequently during 1 hour. If acetylene is present a red precipitate is formed. A large bulb tube or separatory funnel containing glass wool wet with the reagent may also be used.

Transfer the mixture to a beaker and dilute with ammonia water to prevent oxidation. Filter and wash well. Place the precipitate and filter in a tared crucible with a little concentrated nitric acid, ignite, cool, and weigh as copper oxide, or estimate the copper by one of the methods detailed in Chapter VIII. Calculate on the assumption that $(Cu_2C_2H_2)O$ is formed.[27]

Trace amounts of acetylene in air can be estimated by a variation of the Ilosvay test.[28] The acetylene in the air is condensed by use of a liquid-air trap; it is subsequently permitted to evaporate into a gas-sampling bottle; the copper reagent is added, and after development of color on shaking the concentration is determined photometrically.

Apparatus. Condensing coils may be constructed of 18 turns of $^3/_8$-inch standard copper tubing wound on a 1-inch mandrel. The bottom turn leads to a 1- by 2-inch copper chamber, packed with glass wool, to which an exit tube is attached. Simpler traps may also be used. Danger of formation of copper acetylide is negligible at liquid-air temperatures and low acetylene concentrations.

Reagent Test Tube.—Seal a 4-cm. length of glass capillary tubing to

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[25] L. I. Ilosvay, *Ber., 32*, 2698 (1899).

[26] F. P. Treadwell and W. T. Hall, *Analytical Chemistry* (Vol. 2), Wiley, New York. 1915.

[27] W. D. McNally, *Toxicology*, Industrial Medicine, Chicago, 1937.

[28] T. A. Geissman, S. Kaufman, and D. Y. Dollman, *Anal. Chem., 19*, 919 (1947).

a 6-inch test tube. This tube can then be connected to an aspirator bulb with rubber tubing.

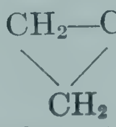
Reagent. Prepare freshly each day analyses are performed. Mix together 10 ml. of 20 per cent copper sulfate solution, 100 g. of $CuSO_4.5H_2O$ dissolved in water and made up to 500 ml.; 60 ml. of hydroxylamine hydrochloride solution, prepared by dissolving 150 g. $NH_2OH.HCl$ in water and made up to 500 ml.; 30 ml. of ammonium hydroxide solution (1:1); 50 ml. of 1 per cent gelatin solution; and 50 ml. of water.

Procedure. Pass the air stream to be analyzed through a drying tower, containing soda lime and indicating Drierite, into the condensing coil, which is immersed in liquid air, and through a wet meter. At flow rates of 4 to 6 cubic feet per hour no detectable amount of acetylene escapes condensation in one coil. After a suitable amount of air has been sampled, connect the exit tube of the coil to the upper nipple of a 300-ml. gas-sample bottle filled with water and supported in a vertical position on a ring stand. Open the stopcocks of the gas-sample bottle. Close the entrance to the condensing coil with a pinch clamp. Remove the coil from the liquid air and place it in a beaker of water. After the coil is warm and water ceases to issue from the sample bottle, open the inlet to the coil and pull air through the coil until all the water has drained from the sample bottle. Close the stopcocks.

Transfer 10 ml. of the copper reagent and 10 ml. of alcohol, which reduces foaming, into the 6-inch test tube. Fit the test tube in an inverted position on the gas-sample bottle by means of a stopper and apply pressure with the aspirator bulb, opening the stopcock long enough to permit the reagent to be forced into the gas-sample bottle. Close the stopcock and shake the gas-sample bottle vigorously for 1 minute, in which time the reagent becomes pink to Burgundy red, if acetylene is present. Transfer quantitatively to a 100-ml. volumetric flask and make up to volume with water. Transfer an aliquot to a colorimeter cell and read the transmission with a 515-mμ filter. Obtain the concentration of acetylene from a standard curve.

D. SATURATED CYCLIC HYDROCARBONS

1. Cyclopropane

Cyclopropane, , trimethylene, propene, is a colorless gas which liquefies under 4 to 6 atmospheres pressure. It boils at —34° C.

One volume of the gas is soluble in about 2.7 volumes of water but it is freely soluble in alcohol, ether, and fixed oils. The lower and upper limits of inflammability of cyclopropane in air are 2.4 and 10.3 per cent by volume, respectively. This substance has been recommended as an anesthetic.

The maximum allowable concentration recommended for this substance is 400 parts of cyclopropane per million parts of air.

Its concentration in air can be determined by the methods detailed in Chapter XII. The gas itself may be assayed by methods detailed in the United States Pharmacopeia.

2. *Cyclohexane*

Cyclohexane is a solvent for resins and rubber. It is employed in resin molding, in wire coating with resins, and as a chemical intermediate. It is also used as a degreasing agent and a paint thinner.

Cyclohexane, C_6H_{12}, has the synonyms hexahydrobenzene, benzene hexahydride, hexamethylene, and hexanaphthene. It is a water-white, noncorrosive liquid. It boils at 80.8° C.; has a specific gravity of 0.779 at 20/4° C.; a refractive index of 1.4273 at 20° C.; with a flammable range of 1.3–8.4 per cent by volume. It has practically the same vapor pressure as benzene. It is insoluble in water but is completely miscible with alcohol, ethers, hydrocarbons, chlorinated hydrocarbons, and most other organic solvents. It is a solvent for a number of resins, rubber, oils, fats, waxes, bitumen, and cellulose ethers.

Cyclohexane is considered to be less toxic than benzene. High concentrations may cause staggering and paralysis. The lethal concentration is of the order of 60–70 mg. per liter. The chronic effects of the inhalation of the vapors of this substance are similar in character to but much weaker than benzene, especially with respect to its action on the blood. The generally accepted maximum allowable concentration for an 8-hour daily exposure is 400 parts of cyclohexane per million parts of air.

The concentration of its vapor in air can be obtained by the use of the general methods detailed in Chapter XII. Thus Treon, Crutchfield, and Kitzmiller,[29] in a study of the physiological response of animals to cyclohexane, methylcyclohexane, and other substances, used a combustible-gas indicator for concentrations of cyclohexane and methylcyclohexane of the order of 0.95 to 2.65 mg. per liter. They determined higher concentrations of the order of 89.6 mg. per liter by means of a Zeiss interferometer. Concentrations of 4.2 to 62.6 mg. per liter were estimated by passing the air sample over a 10-inch-long platinum star in a 1.25-inch fused-silica tube for 10 to 60 minutes at a rate of 100 ml. per minute at a temperature of 850° C., and weighing the resulting carbon dioxide collected on Ascarite.

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[29] J. F. Treon, W. E. Crutchfield, Jr., and K. V. Kitzmiller, *J. Ind. Hyg. Toxicol.*, *25*, 323 (1943).

3. Methylcyclohexane

Methylcyclohexane, $CH_3C_6H_{11}$, hexahydrotoluene, is a colorless liquid with a specific gravity of 0.769 at 20/4° C. It boils at 100.3° C. and has a refractive index of 1.4235. Its uses are analogous to those of cyclohexane. The maximum allowable concentration accepted for methylcyclohexane is 500 parts per million. It may be estimated by the methods described for cyclohexane.

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CHAPTER XIV

Benzene and the Aromatic Hydrocarbons

A. BENZENE HOMOLOGUES

1. Benzene

It is important to remember in considering the practical problem of the use of benzene in industry and its role as a principal industrial hazard that two very distinct types of processes are involved.[1] In such industries as (1) the distillation of coal and coal tar in the production of benzene, (2) the blending of motor fuels, and (3) the chemical industries, including oil extraction, dye and dye intermediates, manufacture of paints, varnishes, and stains, and of paint and varnish removers, benzene is used in large quantities. However, the very nature of the industries mentioned demands that the benzene be kept in a closed pipe-line system, any openings representing a loss of valuable vapors, making the system an inefficient one with a correspondingly large financial loss.

In a second group of processes represented by the use of benzene (1) in the rubber industry, (2) in artificial leather manufacture, (3) in canning, (4) in dry cleaning, (5) in connection with the handling of paints, lacquers, varnishes, and stains, (6) in rapid rotogravure printing and quick-drying printing ink in general, and (7) in the fused-collar industry, benzene is employed chiefly as a solvent or a vehicle. As a step in these industrial processes, it must be removed so as to leave the originally dissolved substances in place or unchanged. The method of removal of the benzene is usually to permit it to evaporate. In most instances. evaporation takes place at room temperature; in some, however, the product or material may be warmed in order to remove the benzene with greater rapidity.

In the first group of processes most benzol poisonings are of the acute type, since they arise from leaks in the closed systems. In the second group of industries the vapors arising when benzene is permitted to evaporate in the workroom atmosphere without adequate ventilation constitute the principal cause of chronic benzene poisoning.

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[1] L. Greenburg, *U. S. Pub. Health Service, Reprint 1096,* (1926).

a. Properties

Benzene, C_6H_6, commonly called benzol, is a colorless, clear liquid with a characteristic pleasant odor in low concentrations and a disagreeable odor in higher concentrations. It boils at 80.1° C.; has a specific gravity of 0.8787 at 15/4° C.; solidifies at 5.5° C.; has a refractive index of 1.5016 at 20° C.; and a flash point of 10–12° C. It is highly inflammable substance, having a lower limit of inflammability of 1.4 and an upper limit of 6.8. Commercial 90's benzene has a lower limit of inflammability of 1.5 and an upper limit of 9.5. About 0.08 g. of benzene dissolves in 100 ml. of water at 22° C. It is miscible in all proportions with alcohol, ether, acetic acid, chloroform, carbon disulfide, carbon tetrachloride, and similar common solvents.

b. Toxicity and Physiological Response

In general, the symptoms and signs of acute poisoning by inhalation of benzene[1] are faintness, dizziness, excitation, pallor and later flushing, weakness, headache, breathlessness, apprehension of death, tightness in the chest, visual disturbances, tremor, weakness in extremities, rapid pulse, cyanosis, unconsciousness or narcosis, collapse, tremor and convulsions, coma, acute mania or delirium preceding sudden death at times, or in other cases death occurring several hours to several days subsequent to exposure. In high concentrations, asphyxiation with death results from respiratory paralysis. When taken by mouth, the usual local signs and symptoms of an acute toxic gastritis are seen in addition to the general systemic manifestations.

Chronic benzene poisoning occurs with greater frequency in cold weather or the winter months when natural ventilation is usually reduced to a minimum by closed windows and doors so that the concentration of benzene in the atmosphere reaches high levels. Atmospheric conditions of temperature and humidity also play an important part At times of high heat and high humidity, other things being equal, spontaneous and sporadic outbreaks are most likely to appear. Young girls are especially predisposed to benzene poisoning, as are also pregnant women.

The early symptoms of chronic benzene poisoning comprise headache, dizziness, malaise, loss of appetite, ready fatigue, shortness of breath, and burning of the eyes, throat, and respiratory membranes. Later, nausea, vomiting, and sensations of chilliness and general weakness with bleeding from the mucous membrane may appear. Hemorrhages, the formation of purpura, and marked blood changes with damage to the nervous system are also signs.

The most characteristic pathological effect of benzene is its destructive influence upon the cells of the blood and the blood-forming organs. The typical result of exposure to benzene vapors is a decrease in white blood cells, and this is often followed by a similar reduction in red cells.

It has been pointed out, however, that too great reliance should not be placed upon leucocyte count *alone* as a rapid means of detecting cases of benzene poisoning.[2] While a leucopenia is a characteristic blood finding in benzene poisoning, it is apparently more frequently found in severe than in early cases; and may occasionally be absent even in the former. A reduction in number and an increase in size of the red blood cells would appear to be more sensitive and earlier signs of intoxication.

Continued exposure to concentrations of benzene in air as low as 100 parts per million is objectionable.[3] Lehmann[4] found that 15 mg. per liter, that is, 4,695 parts per million, produced listlessness and confusion after half an hour, and that 20 to 30 mg. per liter (6,260 to 9,390 parts per million) for a few hours caused loss of consciousness.

Some other figures on the toxicity of benzene are the following. Albaugh[5] states that 42 mg. per liter will kill dogs in 20 minutes. Exposure to 5–10 mg. per liter (1,565–3,130 parts per million) of benzene vapor can be borne for 6 hours without serious symptoms, while exposure to 20–30 mg. per liter for 30–60 minutes will cause immediate or subsequent death.[6] The acute and chronic toxicity of moderate concentrations of benzene and mixtures of benzene, toluene, and xylene is discussed by Svirbely, Dunn, and von Oettingen.[6a]

The maximum allowable concentration of benzene for a daily 8-hour exposure recommended by most governmental hygienists is 35 parts per million[6b]; that recommended by the American Standards Association is 100 parts of benzene per million parts of air, equivalent to 0.32 mg. per liter at 25° C. and 760 mm.

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[2] L. Greenburg, M. R. Mayers, L. Goldwater, and A. R. Smith, *J. Ind. Hyg. Toxicol.*, *21*, 395 (1939).

[3] C. E. A. Winslow, *National Safety Council, Final Rept. Comm. Benzol*, Chicago, 1926.

[4] K. B. Lehmann, *Arch. Hyg.*, *75*, 1 (1911–12).

[5] A. P. Albaugh, *Ohio Pub. Health J.*, *6*, 512 (1915).

[6] F. Flury and F. Zernik, *Schaedliche Gase*, Springer, Berlin, 1931.

[6a] J. L. Svirbely, R. C. Duhn, and W. F. von Oettingen, *J. Ind. Hyg. Toxicol.*, *25*, 366 (1943); *26*, 37 (1944).

[6b] *Ind. Hyg. Newsletter*, *7*, No. 8, 15 (1947); as amended, April, 1948.

Schrenk and co-workers[7] investigated the effect of pure and crude benzene on animals. They found that the response of the animals was characteristic of benzene poisoning and that the physiological effect was due primarily to benzene and not to the impurities.

c. Detection

Benzene is generally detected by conversion to *m*-dinitrobenzene[8] and subsequent detection of the latter compound. Thus for the mere detection of benzene in air, the procedures of Pfeiffer[9] or Elliott and Dalton[10] and Chavassieu and Morel[11] may be combined.

After trapping the air by passage through nitration acid, equal volumes of concentrated sulfuric acid (specific gravity 1.84), and fuming nitric acid (specific gravity 1.5), heat on a water bath for 15 minutes to complete nitration; neutralize the nitration acid, with several volumes of 40 per cent sodium hydroxide solution and then make slightly alkaline; make faintly acid with hydrochloric acid and dilute to 500 ml. to prevent crystallization of sodium sulfate. Extract with 3 successive portions of ether previously washed with a little sodium hydroxide solution. Transfer the ether layers to an evaporating dish and evaporate. A yellowish, crystalline residue indicates the possible presence of dinitrobenzene. To confirm, the following tests may be performed.

Levulose Test.[10-12] Dissolve about 0.35 g. of the residue in 100 ml. of alcohol. Make an aliquot of this solution alkaline with several drops of 40 per cent sodium hydroxide solution and add twice the volume of 1 per cent aqueous levulose solution. An intense violet color develops after 2 minutes and then gradually fades. This test is specific for *m*- and *o*-dinitrobenzene. Both compounds are formed in the nitration of benzene but about 95 per cent is the meta compound while only about 5 per cent of both the ortho and para compounds are formed.

α-Naphthol Test. Transfer about 0.1 g. of the residue to a test tube, add 10 ml. of water and 2 g. of zinc dust. Add concentrated hydrochloric acid drop by drop until a moderate action ensues. Continue the reaction for 10 minutes. In this process *m*-dinitrobenzene is reduced to *m*-phenylenediamine. Diazotize the reduced solution by the addition of a few drops of 10 per cent sodium nitrite solution and add saturated sodium carbonate solution until a precipitate of zinc carbonate is obtained. Then add 3 ml. of a 0.1 per cent alkaline solution of α-naphthol. An intense red-brown color indicating the presence of an aromatic amine is produced. This test is more delicate than the levulose test but is not specific for *m*-dinitrobenzene.

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[7] H. H. Schrenk, W. P. Yant, S. J. Pearce, and R. R. Sayers, *J. Ind. Hyg. Toxicol.*, *22*, 63 (1940).

[8] W. P. Yant, H. H. Schrenk, and P. H. Mautz, *U. S. Bur. Mines Rept. Invest.* 3282 (1935).

[9] O. Pfeiffer, *Chem.-Ztg.*, *28*, 884 (1904).

[10] Elliott and J. Dalton, *Analyst*, *44*, 132 (1919).

[11] Chavassieu and Morel, *Compt. rend.*, *143*, 966 (1906).

[12] M. Peronnet and R. Truhaut, *Bull. soc. chim.*, *53*, 1464 (1933); *Chem. Abstracts*, *28*, 3339 (1934).

Sulfuric Acid-Formaldehyde Method. A simple test for the detection of benzene involves the absorption of the vapor in concentrated sulfuric acid containing formaldehyde; an orange-brown color is produced, even traces of benzene being sufficient for this result. It has been adopted as the British[13] standardized test for the determination of small quantities of the vapor in industry.

The test is carried out by drawing a sample of the atmosphere under consideration through a tube containing the reagent by means of a hand pump of definite capacity, and determining the number of strokes required to produce a certain standard depth of color. From the number of strokes of the pump required to produce the standard color, the concentration of benzene vapor present may be obtained by reference to the table given below.

Effect of Other Vapors. The color produced by benzene with the formaldehyde-sulfuric acid reagent is also given by the vapors of toluene and of coal tar naphthas. The test is slightly more sensitive to toluene than to benzene. While, as noted on pages 469 and 539, benzene is more toxic than toluene, they have roughly the same order of toxicity, hence no distinction[13] is at times made between them for industrial-hygiene purposes, and the error caused by the presence of small quantities of toluene vapor can be ignored in estimating the benzene concentration. For the estimation of toluene vapor alone, a separate calibration of the test and another set of standards is advisable.

This method can only give a qualitative indication of the presence of solvent naphthas, consisting of xylenes and their higher homologues because of their complex and variable composition. Naphthalene vapor interferes by producing a black film on the surface of the reagent.

The vapors of crude benzols which have had only mild refining treatment may contain compounds such as thiophene and unsaturated hydrocarbons in sufficient concentrations to interfere with the test by giving a yellow or red color to the sulfuric acid. Their presence in such concentrations may be detected by pumping the atmosphere through a bubbler containing concentrated sulfuric acid alone, in which case the respective color only will be produced. The quantities of such substances usually associated with commercial grades of benzene are generally insufficient to affect the test.

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[13] *Dept. Sci. Ind. Research, Brit. Leaflet 4* (1939).

The apparatus used is similar to that described for chlorine (page 377) and for carbon disulfide (page 329).

Preparation of Reagent. Transfer 0.5 ml. of 40 per cent formaldehyde solution with a graduated pipette to the bubbler. Make up to 10 ml. volume by the addition of concentrated sulfuric acid. Stir to mix thoroughly.

Preparation of Standard Color. Dissolve 1 g. of sodium nitroprusside, $Na_2Fe(CN)_5NO.2H_2O$, weighed accurately, in water and make up to 100 ml. in a volumetric flask. If the solution is well stoppered and kept in the dark it should last 2 weeks. If any marked change in shade or color occurs it should be prepared again. When required for a test, 10 ml. of this solution is transferred to a tube of the same bore as the bubbler.

Procedure. On entering the atmosphere to be tested, begin to draw the strokes very slowly, using 10 seconds per stroke. Continue the pumping until the depth of color developed is approximately that of the standard color, counting the number of strokes made. Disconnect the bubbler from the train and compare immediately with the standard tube, the two tubes being observed side by side by daylight reflected from a white surface held 2–3 inches behind the tubes.

If the depth of color is the same in both tubes, the concentration can be obtained from the table below. If it is less than the standard, replace the bubbler in the train and continue the strokes until equivalence of color is reached. If the test color is deeper, repeat the test with another aliquot of the reagent, using fewer strokes of the pump.

Concentration	No. of strokes
Up to 1/700	Less than 1
1/700–1/1,200	1–2
1/1,200–1/1,500	2
1/1,500–1/2,000	3
1/2,000–1/2,500	4
1/2,500–1/3,000	5
1/3,000–1/3,600	6
1/3,600–1/4,200	7
1/4,200–1/4,700	8
1/4,700–1/5,300	9

1/5,300–1/6,000	10
1/7,000	12
1/8,000	15
1/10,000	18

The number of strokes required to give the standard color at concentrations lower than those given in the table is roughly inversely proportional to the concentration present; an approximate estimate of the latter may be obtained in such cases, if desired, by carrying out the test in the usual manner and extrapolating from the above figures.

The standard color is given by pure or nearly pure benzene. Crude benzols may give a slightly different shade of color, but this should not interfere with the comparison of the depth of color of the reagent and standard

The test is capable of detecting concentrations down to 0.32–0.35 mg. per liter of air, equivalent to 100 parts per million.

d. Determination

The literature on methods for the determination of benzene is extensive. Few of the methods devised are extremely accurate. However, as discussed in Chapter I, the more important object in benzene analyses is to determine the relative concentrations present in an atmosphere.[14]

One of the more accurate methods is the Smyth modification of the *m*-dinitrobenzene-reduction method. Sampling may be performed in the field but analyses can only be made in the laboratory, for the method is somewhat cumbersome and slow. A more rapid method but less accurate one is the *m*-dinitrobenzene-butanone method. Still another but less accurate method, which is simple and may be performed in the field, is the oxidation method in the presence of hydrogen peroxide and iron salts.[15]

Butanone Method. A general reaction is given by *m*-dinitrobenzene ketones such as acetone, ethyl methyl ketone, methyl propyl ketone, etc., with the formation of violet colors, the intensities of which are proportional to the concentration of *m*-dinitrobenzene. This is the basis for the butanone-ethyl methyl ketone method for the determination of benzene as developed by the U. S. Bureau of Mines.[16,17] The benzene is nitrated

[14] L. Greenburg, *U. S. Pub. Health Service, Reprint 1096* (1926).

[15] W. A. Cook and J. B. Ficklen, *Ind. Eng. Chem., Anal. Ed., 4,* 406 (1932).

[16] H. H. Schrenk, S. J. Pearce, and W. P. Yant, *U. S. Bur. Mines, Rept. Invest. 3287* (1935).

[17] S. J. Pearce, H. H. Schrenk, and W. P. Yant, *U. S. Bur. Mines, Rept. Invest. 3302* (1936).

to form *m*-dinitrobenzene, which is subsequently estimated colorimetrically with the aid of butanone.

Sampling. The samples may be obtained by aspirating the air at 20 to 30 ml. per minute through a bubbler, similar to that shown in Figure 106. containing 2 ml. of nitrating acid consisting of equal parts of concentrated sulfuric acid (specific gravity 1.84) and fuming nitric acid (specific gravity 1.5) by some appropriate means such as a calibrated rubber aspirating bulb or motor-driven exhaust pump and flowmeter; or the sample may be collected in vacuum bottles and subsequently displaced through the nitrating acid in the same bubbler device, by means of mercury displacement at the same sampling rate. For a concentration of benzene of 25 parts per million a 500-ml. air sample is sufficient.

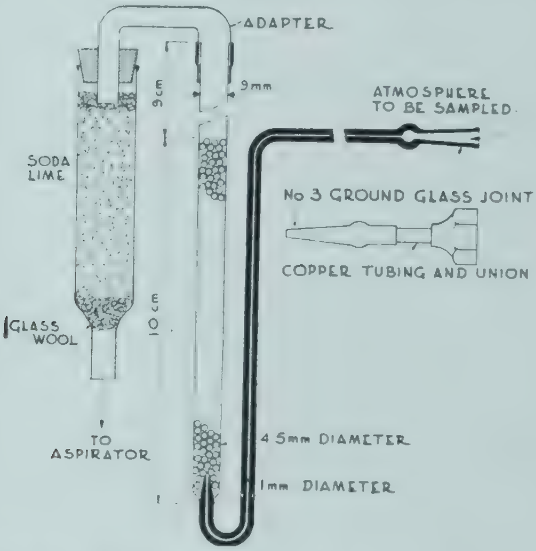

Fig. 106. Bubbler for nitrating benzene or toluene vapor-air mixtures.[17a]

Procedure. Allow the solution to stand for 30 minutes for nitration to be complete. Transfer the acid and beads to a 100-ml. flask. Rinse the absorber with five 1-ml. portions of water and add these washings to the sample solution in the flask. Cool the sample solution to 0–20° C. and slowly neutralize by the addition of a 40 per cent sodium hydroxide solution, using a piece of litmus paper as indicator. Add 1 to 2 drops in excess, as a yellow color will develop if even a slight acidity is present. Warm the sample solution to 25–30° C., which prevents crystallization of salts, and add 10 ml. of butanone. Shake occasionally for 10 minutes. Transfer to an ordinary burette having a funnel top containing a jagged piece of glass which will allow the liquid to pass but will retain the glass beads. After the layers separate, draw off the water layer and then transfer the ethyl methyl ketone layer to a suitable colorimeter tube. Add 1.5 ml. of 40 per cent sodium hydroxide solution to the solvent solution. Shake vigorously for several minutes and occasionally for 1 hour while the color develops. During the period of color development protect from exposure to light. Compare with a series of standards.

[17a] After W. P. Yant, S. J. Pearce, and H. H. Schrenk, *U. S. Bur. Mines, Rept. Invest. 3323* (1936).

If the color extracted is too intense for comparison, separate the butanone layer and measure the volume accurately. Dilute an aliquot portion with ethyl methyl ketone to the volume noted. If the aliquot portion is 1 ml. or less, add 0.7 ml. of an aqueous solution containing 1.7 per cent of sodium nitrate and 0.86 per cent of anhydrous sodium sulfate, in order to keep the ionic strength of the solution the same. As the volume of the aliquot taken increases, reduce the amount of nitrate-sulfate solution added for this purpose. Then add 1.5 ml. of 40 per cent sodium hydroxide solution to the diluted and adjusted aliquot and proceed as directed.

Modified Method. This method of sampling and procedure was modified by Siegel and Burke[18] in order to enable the analyst to handle large numbers of samples simultaneously. Samples of air are taken by means of air displacement, using separatory funnels ranging in size from 100 to 800 ml., depending on the concentration of benzene vapor expected. These funnels must be thoroughly degreased and the stopper and stopcock relubricated by the use of graphite.

Air may be drawn through the funnels with the aid of a hand pump and the separatory funnel must be well flushed with the air to be sampled in order to insure a proper specimen. The stopcocks and stoppers are closed and the samples are taken to the laboratory for analysis.

Procedure. Cool the air sample in the separatory funnel and carefully add 2 ml. of the sulfuric acid-fuming nitric acid nitrating mixture through the stem of the funnel. Close the stopcock, and wet the entire interior of the funnel by rotation. Allow the separatory funnel to remain on its side overnight. In the morning immerse the funnel in a beaker of ice water, and dilute with 5 ml. of water. Then neutralize with 40 per cent sodium hydroxide solution. Add a slight excess of 40 per cent sodium hydroxide solution and then add 10 ml. of ethyl methyl ketone. Shake the contents of the flask, allow to stand so that the immiscible layers may separate, and, after complete separation, draw off the aqueous layer and discard. Transfer the ethyl methyl ketone layer to a 50-ml. Nessler comparison tube and add 1.5 ml. of 40 per cent sodium hydroxide solution. Compare with prepared standards to ascertain the quantity of dinitrobenzene or benzene.

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[18] J. Siegel and W. J. Burke, *N. Y. State Ind. Bull. 18,* 17 (1939).

Standards. Dissolve 0.1076 g. of *m*-dinitrobenzene in 100 ml. of the sulfuric acid-fuming nitric acid nitration mixture. Each ml. of this mixture is equivalent to 0.50 mg. of benzene. Dilute 10 ml. of this mixture to 100 ml. Each ml. of this dilution is equivalent to 0.05 mg. of benzene. The standard is stable for a few months.

To prepare a series of standards containing 0.01–0.06 mg. of benzene at 0.01 mg. intervals, pipette the proper aliquots of the stock standard solution into glass-stoppered bottles. Dilute to 2 ml. with the nitrating acid. Add 5 ml. of water and complete the color development in the same way as for the test sample.

Alternative methods for the preparation of standards from benzene solution in medicinal mineral oil and water have been described.[19,20] The accuracy of the method does not warrant such labor in the preparation of precise standards.

Dolin Modification. The butanone method for benzene has been modified by Dolin.[20a] In the method detailed above, the color that results when benzene is present is stable in the presence of acetic acid, while the colors assumed by toluene, xylene, ethylbenzene, chlorobenzene, and analogous substances disappear rapidly.

Procedure. Treat 0.1 ml. of the liquid to be tested or a known volume of air in a separatory funnel with 2 ml. of a mixture of equal volumes of concentrated sulfuric acid and fuming nitric acid. After 10 minutes, add 25 ml. of water and cool the mixture. Extract the nitrated material with 25 ml. of ether. Wash the ether extract with 25 ml. of water, and transfer the ether extract to a 100-ml. volumetric flask. Make to volume with 95 per cent alcohol. Transfer a 10-ml. aliquot to a test tube, add 1 ml. of butanone and 2 drops of 40 per cent sodium hydroxide solution, shake the mixture, and allow to stand for 10 minutes. If benzene is present in the original solution or air, a crimson color will appear. Add 5 drops of glacial

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[19] W. P. Yant, H. H. Schrenk, and P. H. Mautz, *U. S. Bur. Mines, Rept. Invest.* 3282 (1935).

[20] S. J. Pearce, H. H. Schrenk, and W. P. Yant, *U. S. Bur. Mines, Rept. Invest.* 3302 (1936).

[20a] B. H. Dolin, *Ind. Eng. Chem., Anal. Ed.*, 15, 242 (1943); *N. Y. State Ind. Bull.*, 25, No. 7 (1946).

acetic acid, agitate the test tube, and allow to stand for an additional 10 minutes. At the end of this period compare with known concentrations of benzene similarly treated or obtain the transmission and calculate the amount of benzene from a standard curve. If the original test mixture contains considerable xylene, the residual yellow color due to this component may be compensated for by backing the comparison tubes with dilute solutions of potassium dichromate.

***m*-Dinitrobenzene Reduction Method.** This method is based on the nitration of benzene with the formation of *m*-dinitrobenzene, which is separated from the nitrating acids by steam distillation. The *m*-dinitrobenzene is then reduced by an excess of standard titanous chloride solution and is estimated by titration of the excess titanous chloride solution with standard ferric alum solution. The reactions are

$$C_6H_6 + 2HNO_3 \longrightarrow C_6H_4(NO_2)_2 + 2H_2O$$

$$C_6H_4(NO_2)_2 + 12TiCl_3 + 12HCl \longrightarrow C_6H_4(NH_2)_2 + 12TiCl_4 + 4H_2O$$

$$2TiCl_3 + 2HCl + Fe_2(SO_4)_3 \longrightarrow 2TiCl_4 + 2FeSO_4 + H_2SO_4$$

This method is the Smyth[21,22] modification based on the work of Pfeiffer,[23] Elliott and Dalton,[24] and English.[25]

Reagents. Nitrating Acid.—Mix equal volumes of concentrated sulfuric acid and fuming nitric acid (specific gravity 1.5).

Ferric Alum Solution.—Dissolve 24.2 g. of ferric ammonium sulfate, $Fe(NH_4)(SO_4)_2.12H_2O$, in water containing 20 ml. of concentrated sulfuric acid and then dilute to 1 liter with recently boiled and cooled water. This solution is approximately 0.025 *M*.

Titanous Chloride Solution.—Add 7 ml. of reagent 20 per cent titanous chloride solution and 150 ml. of concentrated hydrochloric acid to water and dilute to 1 liter with recently boiled and cooled water. Pass a slow stream of hydrogen gas through this solution for 24 hours before use and store the reagent solution under slight pressure of hydrogen gas from a Kipp generator or from a cylinder of hydrogen gas. The burette from which the titanous chloride solution is delivered must also be connected with the hydrogen supply, as in the arrangement described by English.[25,26] This solution is approximately 0.1 *M*.

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[21] H. F. Smyth, *J. Ind. Hyg.*, *11*, 338 (1929); *13*, 227 (1931).

[22] H. F. Smyth and H. F. Smyth, Jr., *J. Ind. Hyg.*, *10*, 163 (1928).

[23] O. Pfeiffer, *Chem.-Ztg.*, *28*, 884 (1904).

[24] Elliott and J. Dalton, *Analyst*, *44*, 132 (1919).

[25] F. L. English, *Ind. Eng. Chem.*, *12*, 994 (1920).

[26] E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*. Longmans, Green, London, 1918.

Standardization of Solutions. First check the ferric alum solution against the titanous chloride solution. Place 100 ml. of water in a wide-mouthed flask, add 1 g. of sodium bicarbonate, and continue with the procedure outlined below under the section *Titration*, beginning with the words, "fit the flask with a two-hole stopper." Use 10 ml. of the titanous chloride solution, and calculate the strength of the ferric ammonium sulfate solution in terms of the titanous chloride solution, as, for instance. 1 ml. of ferric alum solution is equivalent to 0.54 ml. of the titanous chloride solution.

Standardize the titanous chloride solution against a solution of recrystallized *m*-dinitrobenzene in concentrated sulfuric acid. A convenient strength for this standard is 2 g. per liter. Run a measured volume of the *m*-dinitrobenzene solution into 100 ml. of water in a wide-mouthed flask, add 5 ml. of a saturated solution of sodium bicarbonate in water, and then proceed with the titration beginning at the point, "Fit the flask with a two-hole stopper. . ." (page 535), except that no 40 per cent sulfuric acid is added. Calculate the strength of the titanous chloride solution in terms of benzene, 1 g. of dinitrobenzene is equivalent to 0.4654 g. of benzene. One equivalent of benzene is equivalent to 12 of titanous chloride and 1 of ferric alum is equivalent to 2 of titanous chloride. The titanous chloride solution may also be standardized against recrystallized *p*-nitroaniline.

Sampling. The sampling apparatus consists of an absorption device (Fig. 107) connected by glass tubing with the exact spot at which the air sample is to be taken and an aspirating bottle or equivalent device to draw the air through the absorber. When there is much organic dust in the air, a cotton filter should be inserted in the tubing before the absorber. The aspirator (Fig. 18) is placed on a box or shelf and the volume of air sample collected is measured on a scale down the outside of the bottle by the fall in water level.

An aspirator is recommended by Smyth, even though it is known to be less accurate in measuring the sample than is the final determination. because it permits the sampling to continue uniformly over a moderately long time. This yields a sample representing average working conditions and eliminates the effect of short variations in vapor production. For grab samples the devices described in Chapter II may be used. When sample bulbs are used, the bulb can be transported to the laboratory, where the sample of air containing the benzene can be passed through the absorption device shown in Figure 107, either by displacing the air sample from the bulb with mercury or water or by rinsing it out with pure air.

After placing the aspirator and sampling line in position, fill the absorber with 10 ml. of the nitrating acid and place it in a clamp fastened to the aspirator bottle. Start the water running from the aspirator bottle and regulate the flow so that a stream of air is drawn through the acid at a rate close to 2.4 liters per hour. Usually a sample between 1 and 2 liters is adequate.

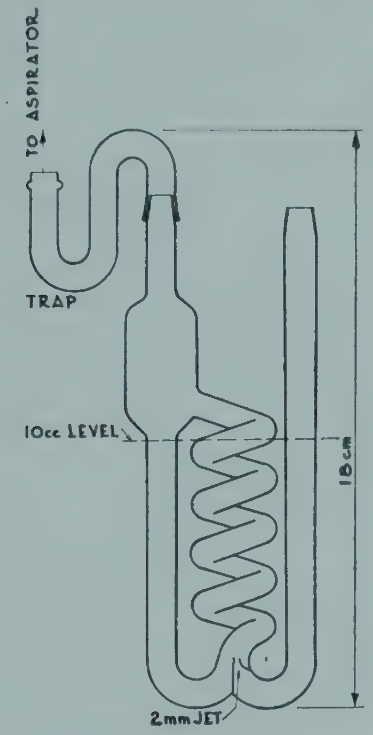

Fig. 107. Bubbler used for the absorption of benzene vapors in nitration acid.

After the air has been passed through the acid, disconnect the absorber and rinse the acid into a glass-stoppered bottle for transportation to the laboratory. The rinsing should be done with a fresh lot of the same acid used for the absorption, since this obviates the necessity of drying the absorber before another sample is taken. The absorber is easily emptied if a rubber tube is attached to the entrance side and is blown through, with the absorber inverted or still better a rubber aspirator bulb may be attached and used for the blowing-out process. The acid is usually colorless after a sample has been taken when toluene is absent, although sometimes a pale-yellow color is seen. The determination may be made at any convenient time, as no change affecting the benzene compounds takes place on storage of the acid solution. (Toluene samples must be diluted as soon as sampling is completed to obtain accurate results for toluene.)

Procedure. Distillation. In the laboratory, wash the nitrating acid containing the benzene as dinitrobenzene into 20 ml. of water in the flask of a steam-distillation apparatus resembling that shown in Figure 108. No special precautions need be taken in this washing if the flask is made of Pyrex or other heat-resistant glass, since the amount of acid involved is small. Cool the diluted acid and carefully neutralize with 40 per cent sodium hydroxide solution. When the mixture is nearly neutral, add 1 ml. of a 1 per cent *aqueous* phenolphthalein suspension, and continue the addition of alkali until one drop turns the solution red. Add 25 g. of anhydrous sodium sulfate and make up the volume of the solution to approximately 150 ml.

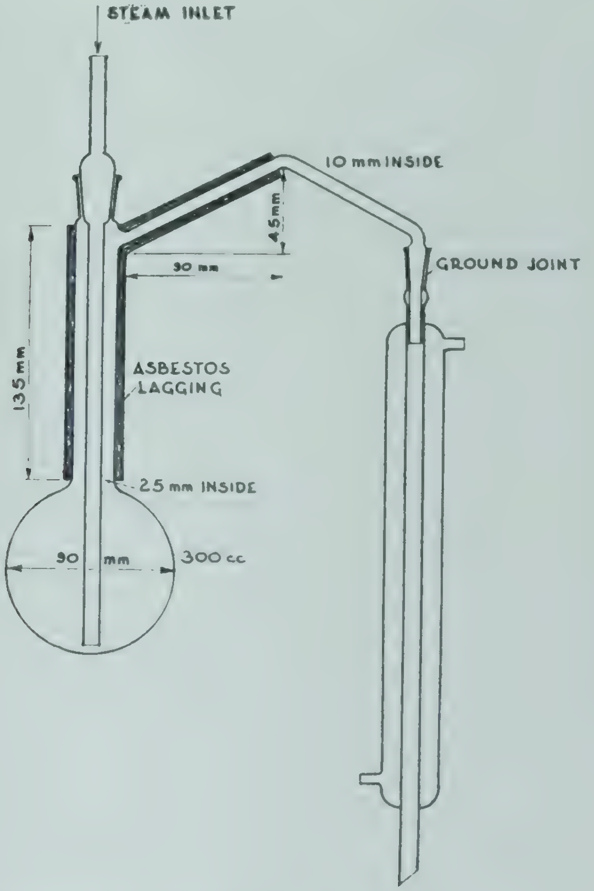

Fig. 108. Steam distillation apparatus used for the determination of benzene in air.

Heat the flask rapidly until refluxing starts, then reduce the heat until the volume remains approximately constant while steam is admitted at such a rate that the distillate is close to 5 ml. per minute. It is convenient to use an electric heater controlled by calibrated rheostats, or calibrated gas flames. Collect 100 ml. of distillate in a 250-ml. wide-mouthed flask of heat-resistant glass. If crystals separate in the condenser during the first part of the distillation, it is well to turn off the cooling water until the hot distillate washes them down into the receiver. When these crystals form, it is necessary to collect 150 ml. of the distillate, as they indicate that a large amount of the nitro compound is present. In this case, the distillate should be titrated in two portions. In the absence of toluene no change from the first phenolphthalein red color is seen on distillation, and the distillate is usually colorless.

Titration. Add 1 g. of sodium bicarbonate to the distillate and fit the flask with a two-hole stopper, through one hole of which a rapid stream of carbon dioxide is admitted to exclude the oxygen of the air. This stream can well come from a cylinder of the compressed gas, since the small amount of oxygen present in the commercial gas will generally not interfere with the results. If carbon dioxide is not available, oxygen-free natural gas or nitrogen can be used. Arrange the gas-delivery line with a water-sealed pressure release, so that the flask containing the distillate can be stoppered tightly, thus making readjustment of the gas supply unnecessary. Either a stream of carbon dioxide or a small positive pressure of the gas must be maintained throughout the titration.

Add 25 ml. of 40 per cent sulfuric acid through the second hole of the stopper, and then close the hole with a glass plug, the carbon dioxide being permitted to escape through the release mentioned above. Place the flask in a boiling-water bath for 5 minutes; add an amount of standardized titanous chloride solution estimated to be at least 10 ml. in excess of the amount to be consumed by the dinitrobenzene, and return the flask to the boiling water bath for 10 minutes.

In the presence of much dinitrobenzene, the purple color of the solution becomes much deeper during the heating. It is better to add too much titanous chloride excess than too little. Experience will tell what the excess should be.

After the heating, run the ferric ammonium sulfate solution in, at once, until the purple color is practically discharged. Add 10 ml. of 10 per cent potassium or ammonium thiocyanate solution and continue the addition of ferric alum solution until one drop produces a red color which persists for 1 minute. Maintain the stream of carbon dioxide throughout the entire titration. From the known strengths of the titanous chloride solution and ferric ammonium sulfate solution, standardized as directed above, calculate the weight of benzene and express the concentration of vapor in milligrams per liter. The latter figure multiplied by 313 gives parts per million by volume.

Calculation. Suppose that 10.02 ml. of titanous chloride solution were found to be equivalent to 18.38 ml. of ferric alum solution; then 1 ml. of ferric alum solution is equivalent to 10.02/18.83, or 0.545 ml. of titanous chloride solution.

Suppose that 20 mg. of dinitrobenzene and 31.16 ml. of titanous chloride solution were found to be equivalent to 20.26 ml. of the same ferric ammonium sulfate solution as above; then the excess of titanous chloride solution present was 20.26 × 0.545, or 11.05 ml.; and the titanous chloride actually used in reducing the dinitrobenzene was 31.16 — 11.05, or 20.11 ml.; and 1 ml. of titanous chloride solution equals 20 mg./20.11 ml., or 0.994 mg. of dinitrobenzene; which is the same as 0.994 × 0.4654, or 0.463 mg. of benzene.

Then, if the distillate from one air sample was equivalent to 20.02 ml. of titanous chloride solution and 19.18 ml. of ferric alum solution, the same solutions as standardized above, there was an excess of 19.18 × 0.545, or 10.45 ml. of titanous chloride over the amount consumed in reducing the dinitrobenzene from the air sample; and the titanous chloride solution actually used in this reduction was 20.02 — 10.45, or 9.57 ml.; and the distillate contained 9.57 × 0.994, or 9.50 mg. of dinitrobenzene; and the air sample contained 9.57 × 0.463, or 4.43 mg. of benzene.

If the volume of the air sample was 2.3 liters, then the concentration of benzene in the air was 4.43/2.3, 4.43 mg./2.3 liters, or 1.9 mg./liter; which is the same as 1.9 × 313, or 595 parts per million by volume.

Ethyl alcohol and mixtures of ethyl, butyl, and amyl alcohols and acetates do not interfere. Petroleum ether and gasoline do not interfere unless they contain olefins or benzene. Toluene may be estimated by the method as described with an accuracy of 50 to 90 per cent. If toluene is present, to obtain more accurate results for benzene, the method must be followed as outlined below.

Where points of the procedure are not mentioned, it is understood that they remain as described above.

(1) The nitration acid through which the air sample has been passed may be stored any length of time desired before analysis, but before dilution it must be heated 30 minutes in a boiling-water bath. When toluene is present, this acid is usually yellower than when it is absent.

(2) After dilution of the acid, the neutralization must be made with great care, the last few drops of alkali being much diluted to avoid passing the end point. A red-brown color is developed before the phenolphthalein end point is reached. Then buffer the solution to a pH of 12.3 by the addition of 50 ml. of a concentrated buffer solution, made from 14.885 g. of highly purified boric acid and 300 ml. of carbonate-free exactly normal sodium hydroxide solution dissolved in recently boiled water and made to 1 liter. After cooling to room temperature make up the distillation mixture to 150 ml.

(3) Heat the buffered solution in the distillation apparatus so that it starts to reflux in 15 minutes and continues to reflux, but does not start to distill for 15 minutes more. The color becomes dark mahogany during the refluxing. Then admit steam and continue the distillation and titration as described for benzene alone. The distillate is colored pale yellow when much toluene is present but this does not interfere with the titration.

Oxidation Method with Hydrogen Peroxide and Iron Salts.[27,28] This method is based on the production of a reddish-brown color and black precipitate by the addition of 5 ml. of 0.5 per cent ferrous sulfate solution and 2 ml. of 1 per cent hydrogen peroxide solution to as little as 0.01 ml. of benzene. The reddish-brown color is produced with these reagents with as little as 0.005 ml. of benzene.

Apparatus. Fill with glass beads a 125- by 20-mm. Pyrex U-tube equipped with ground-glass stoppers an dside arms with No. 5 interchangeable ground-glass connections. Mount in a wooden box which has a hinged front so that solid carbon dioxide may be packed around the U-tube. The top of the box should be constructed so that the U-tube can be removed easily for immersion in hot water when a determination is to be made.

Sampling. In collecting the sample of air for benzene vapor, the inlet of the U-tube is held at the location where the sample is to be taken without any preliminary train for removal of water vapor or other materials. If it is desired to sample air at a point that cannot be conveniently reached by the side arm of the U-tube, an extension tube with a No. 5 interchangeable ground-glass connection can be attached to the U-tube. By this means benzene vapor does not come in contact with any rubber tubing, and errors from this source are avoided. After collecting the sample, turn the glass plugs to the closed position. Graphite should be used as the lubricant for all ground-glass surfaces to prevent absorption which might result from the use of the usual type of lubricants. After collecting the sample, the U-tube may be replaced by another U-tube for collection of the next sample. Another point to observe is that if the glass surface is increased through the use of a larger tube and more glass beads, the rate of air flow during the sampling operation can be correspondingly increased and hence the time of sampling shortened.

Benzene vapors may be quantitatively retained by this method of sampling if the rate of air flow is maintained at 2 liters per minute.

Apparatus. The U-tube in which the sample is collected is connected to a suitable bubbler unit containing 25 ml. of water for the removal of the more water-soluble vapors, which would otherwise interfere with the test reaction. This bubbler is in turn adjoined to a trap, the inlet tube of which is provided with an opening which is kept closed by means of a glass stopper while the sample is being drawn through the apparatus. This trap is immersed in a solid carbon dioxide-acetone cooling mixture contained in a Dewar flask. Following the trap is a flowmeter, connected to a suction line so that the rate of air flow may be known.

Procedure. Immerse the U-tube in hot water, kept at 80–90° C. to insure complete vaporization of the collected sample. At the same time draw air through the apparatus at the rate of 1/3 of a liter per minute. A period of 5 minutes is generally sufficient to volatilize and sweep the sample through the apparatus, the benzene together with a small portion of less water-miscible solvents being frozen out in the trap. Discontinue the suction and remove the stopper of the inlet tube of the trap.

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[27] W. A. Cook and J. B. Ficklen, *Ind. Eng. Chem., Anal. Ed., 4,* 406 (1932).
[28] W. A. Cook and J. B. Ficklen, *J. Ind. Hyg., 17,* 43 (1935).

Add 5 ml. of 0.5 per cent solution of ferrous sulfate, followed immediately by 2 ml. of 1 per cent hydrogen peroxide solution through the inlet tube. These solutions should be made up just prior to running a series of determinations, care being taken that the hydrogen peroxide used is from fresh stock. Remove the trap from the freezing mixture and air line. Stopper with an interchangeable glass ground stopper, shake vigorously for 2 minutes, and pour the contents into a test tube. If benzene is present in an amount of 0.005 ml., the characteristic brown coloration is produced in 2 to 5 minutes after the reagents are added. If 0.010 to 0.050 ml. are present, then in addition to the brown coloration a black amorphous precipitate is formed.

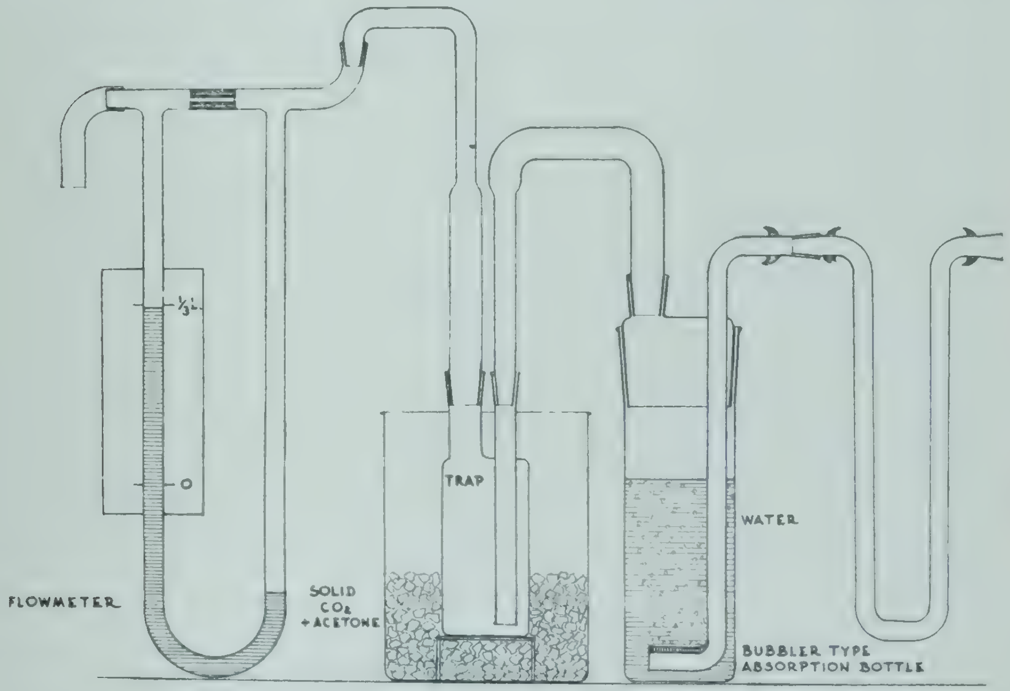

Fig. 109. Apparatus for trapping benzene by freezing.

Dissolve the black amorphous precipitate by the addition of 1 ml. of 2 *N* nitric acid. This solution may be diluted with water and compared with standards prepared from known volumes of benzene.

This reaction is very complicated, yielding a mixture of phenol, catechol, hydroquinone, and the black amorphous precipitate. Therefore the colors of the resultant liquid cannot lend themselves to more than an approximate quantitative estimation except over the narrow range from 0.010–0.050 ml. of benzene.

Cook and Ficklen[27] state that toluene, xylene, methyl, ethyl, isopropyl, *n*-butyl, isobutyl, and *n*-amyl alcohols do not appear to interfere. They also found that ethyl acetate, ethyl propionate, *n*-butyl acetate, isoamyl acetate, ethylene chloride, trichloroethylene, tetrachloroethane, carbon tetrachloride, acetone, Cellosolve, and gasoline did not interfere. Nor did mixtures of these solvents disturb the reaction. Solvents boiling much higher than benzene do not come over in the vaporization.

If carbon disulfide is present, amorphous sulfur is liberated. This is not dissolved on the addition of nitric acid and the solution must be filtered in order to be freed from the sulfur precipitate. After filtration, benzene may be estimated from the coloration of the filtrate as detailed above.

2. *Toluene*

The hazards encountered in the industrial use of toluene are similar to those detailed for benzene. It is used extensively in the manufacture of benzoic acid, benzaldehyde, explosives, dyes, and other organic compounds. It is used as a solvent for the extraction of various materials and is also widely used as a diluent in cellulose ester lacquers. It is not a solvent for cellulose esters, but these substances will remain in solution with a greater proportion of toluene as the diluent than with other diluents.

Toluene, $C_6H_5CH_3$, commonly known as toluol, is a colorless liquid with a benzene-like odor. It boils at 110.6° C.; has a specific gravity of 0.866 at 20/4° C.; has a refractive index of 1.4893 at 24° C.; and a flash point of 6–10° C. It has a lower limit of inflammability of 1.3 and an upper limit of 6.8. It is very slightly soluble in water and is miscible with alcohol, chloroform, ether, acetone, glacial acetic acid, etc.

Toluene is considered by many to be relatively nontoxic. This belief is not justified. The effects of exposure to toluene in industry have been discussed by Greenburg and co-workers.[29] Toluene is less dangerous and less volatile than benzene, therefore there is less likelihood of harmful concentrations under equivalent working conditions in comparison with benzene. Exposure to air concentrations much greater than 100 parts per million may result in damage similar to that produced by benzene.[30] The generally accepted maximum allowable concentration is 200 parts of toluene per million parts of air by volume, which is equivalent to 0.752 mg. per liter of air at 25° C. and 760 mm.[31–33]

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[29] L. Greenburg, M. R. Mayers, H. Heimann, and S. Moskowitz, *J. Am. Med. Assoc., 118,* 573 (1942).

[30] W. J. Burke, *N. Y. State Ind. Bull. 17,* 314 (1938).

[31] *Ind. Hyg. Newsletter, 7,* No. 8, 15 (1947).

[32] *Am. Standards,* Z37.12–1943.

[33] W. F. von Oettingen, P. A. Neal, D. D. Donahue, J. L. Svirbely, H. D. Baernstein, A. R. Monaco, P. J. Valaer, and J. L. Mitchell, *U. S. Pub. Health Bull.* 279 (1942).

a. Detection

Toluene may be detected by a general reaction for hydrocarbons.[34,35] On the addition of concentrated sulfuric acid and a few drops of benzal chloride, toluene gives a characteristic light-yellow color. Toluene also gives the sulfuric acid-formaldehyde test described in detail for benzene, page 525. The butanone reaction described in detail below may also be used for its detection.

b. Determination

Butanone Method.[36] The toluene in liquid or vapor phase is nitrated with fuming nitric acid. The acid is then diluted with water, neutralized, extracted with one 10-ml. portion of butanone and 1.5 ml. of 50 per cent potassium hydroxide solution is added to the butanone extract. A blue color turning to violet develops, the intensity of which is proportional to the quantity of toluene nitrated. A series of standards containing known quantities of toluene that have been nitrated in the same manner are prepared simultaneously for color comparison.

Sampling and Apparatus. The toluene vapor-air samples may be taken directly from the atmosphere through 2 ml. of fuming nitric acid, specific gravity 1.50, in a bubbler of the type shown in Figure 106. The soda lime tube prevents acid fumes from reaching the aspirating device. The sample may be collected with a calibrated rubber aspirating bulb, a motor-driven exhaust pump and flowmeter, an equivalent aspirating device, or it may be collected in a vacuum bottle. If the latter method is used, the sample may subsequently be displaced through the nitrating acid with mercury. If collection of a sample from an inaccessible point is desired, the vapor-air mixture is led to the nitration bubbler through approximately 3/16 inch, O. D., flexible copper tubing. Figure 106 shows a method of connecting the copper tubing to the bubbler that is convenient and prevents breakage. It consists of a short nipple of the copper tubing with the male part of a Pyrex interchangeable ground-glass joint sealed to one end and a compression coupling fitted to the other end. Although the copper can be fused directly to the glass, the connection may also be made by using a cement such as De Kotinsky or Insalute. After the copper sampling tube is placed in position, the connector is attached to

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[34] E. Lippmann and I. Pollak, *Monatsh., 23*, 670 (1902).

[35] Merck Index (5th ed.), 1940.

[36] W. P. Yant, S. J. Pearce, and H. H. Schrenk. *U. S. Bur. Mines, Rept. Invest. 3323* (1936).

the tube by means of the coupling and the nitration bubbler is connected by means of the ground-glass connection. Before a sample is taken the copper tubing must be well flushed with the atmosphere to be examined. This may be done by connecting the copper sampling tube directly to the aspirating device. As rubber absorbs toluene vapor, it cannot be used for sampling lines or connections.

Procedure. After the sample is nitrated, transfer the acid and beads to a small flask or bottle fitted with an unlubricated glass stopper and wash the bubbler with six 1-ml. portions of water, which are added to the acid and beads. The samples may be kept in this condition for 1 to 2 weeks before analysis at this point, if desired. The acid solution is neutralized in a water bath at 25–30° C. by slow titration with a 50 per cent solution of potassium hydroxide, 500 g. of potassium hydroxide, KOH, made up to 1 liter with water. A small piece of litmus paper may be used as the indicator. Add an excess of 2 to 3 drops of the alkali solution.

Add 10 ml. of ethyl methyl ketone to the solution and shake occasionally for 10 minutes. It is important at this stage that the bottle and contents be kept warm, at about 25–30° C., to prevent salts from crystallizing and interfering with the quantitative separation of the butanone layer. Transfer the liquid to an ordinary 50-ml. burette to separate the butanone from the aqueous layer. The burette should have a funnel or flared top over which the bottle can be inverted and the "coin"-type stopper loosened to permit the transfer of the liquid but prevent the glass beads from dropping into the burette. An uneven piece of glass may also be used as illustrated in Figure 50. Allow to stand until the layers separate and using the burette as a separatory funnel, draw off the water layer. Transfer the butanone extract to one of a series of 100-ml. Nessler tubes and add 1.5 ml. of 50 per cent potassium hydroxide solution. Shake the tubes vigorously for several minutes and occasionally during the 1 to $1^1/_2$ hours while the color is allowed to develop in the butanone layer.

Preparation of Standards. Prepare a set of standards along with the samples. Prepare the stock solution by breaking a small, thin-walled glass bulb that contains a weighed quantity of toluene (10–20 mg.) under the surface of 10 ml. of fuming nitric acid, specific gravity 1.5, contained in a 25-ml. volumetric flask. Use a glass rod 25 cm. long and 3 mm. in diameter, mushroomed at one end to about 6 mm. in diameter and bent at an angle of 10–15° at a point 3.5 cm. from the mushroomed end, to submerge and break the bulb. Care should be taken to crush the tip of the bulb also, as it contains an appreciable quantity of the liquid toluene.

Remove the rod and place it across a clean beaker so that the wet end remains untouched. Stopper the flask as rapidly as possible and then shake it occasionally for 1 hour, after which wash the acid on the rod into the flask with a few ml. of cold water. Cool the flask and bring the volume of the liquid slowly to the calibration mark by successive additions of water, with cooling between each addition.

Prepare a solution for making a series of comparison standards by diluting a portion of the stock solution with a cooled mixture of 2 parts by volume of fuming nitric acid and 3 parts by volume of water so that 1 ml. of the final solution contains the equivalent of 0.20 mg. of toluene. A standard solution prepared in this manner may remain unchanged for a month.

Comparison standards ranging from 0.05 to 0.25 mg. of toluene at intervals of 0.05 mg. give a good, easily distinguishable gradation of reddish blue. Prepare these standards by pipetting the required aliquots of the standard solution into glass-stoppered bottles. As it is essential that the quantities of acid and water in the standards and samples should be the same, the amount of acid present in the standard is made up to a total of 2 ml. of fuming nitric acid, which is the quantity used in sampling, remembering that 1 ml. of the standard solution contains 0.4 ml. of fuming nitric acid and 0.6 ml. of water. Add enough water to make a total of 6 ml. of water; that is, the final volume of acid and water is 8 ml. The remainder of the procedure for preparing the standards for comparison is the same as that described for the analysis of samples.

Procedure for Making Color Comparisons. The colors are compared by looking horizontally through the tubes and not vertically, as is usually done with Nessler tubes. The best results are obtained by interposing a piece of flashed opal glass between the source of light and the comparator block containing the tubes. The colors may also be compared by holding the tubes against a white background with the light source behind the observer.

Adjusting Samples to the Range of Color Standards. If, during the first 10 minutes of shaking the samples and standards, the color developed by a sample is seen to be too intense for comparison with the standards, the colored butanone layer is separated from the potassium hydroxide layer in a burette calibrated to the tip in order to measure accurately the quantity of butanone. An aliquot portion of the butanone is then diluted with fresh butanone to the previous volume. If the aliquot is 1 ml. or less, add 0.45 ml. of 3.5 per cent potassium nitrate solution, 3.5 g. of potassium nitrate, KNO_3, dissolved in water and make up to 100 ml., to the butanone solution and shake. As the volume of the aliquot is increased the volume of the potassium nitrate solution is decreased proportionately. Then add the usual 1.5 ml. of 50 per cent potassium hydroxide solution and shake. If the color developed is still too intense, this procedure may be repeated. Addition of the potassium nitrate is necessary because without the presence of this salt the color produced is abnormally intense and the results are 10 to 20 per cent high.

If it is known from the odor or general knowledge of the prevailing conditions at the time of sampling that the amount of toluene sampled is more than the highest standard, another procedure may be followed. The acid-water mixture containing the sample may be diluted as much as is desired with a measured volume of a cooled mixture of equal volumes of concentrated nitric acid and water. An aliquot portion of the resulting solution is treated as described above for standards. The neutralized solution may also be diluted with water and an aliquot taken. The latter procedure is limited by the low solubility of the nitrated products of toluene in water. If precipitation of these compounds occurs, the sample may be saved by extracting it with butanone and following the procedure described previously for diluting samples with butanone.

Recrystallized 2,4-dinitrotoluene cannot be used for making the standards for comparison because in the nitration of toluene other nitro products than this compound are formed and a different quality of color is therefore obtained with the pure 2,4-dinitrotoluene.

Compounds that give a similar color to toluene by this method are benzene, ethylbenzene, chlorobenzene, and xylene. Of these compounds, benzene and xylene are the more important from the standpoint of interference. The color produced by nitrating liquid xylene has approximately 1/10 the intensity of the color produced by an equal weight of toluene. Both liquid ethylbenzene and chlorobenzene produce colors equivalent in intensity to an equal weight of benzene. However, the colors differ in quality from that produced by toluene. That produced by ethylbenzene is somewhat redder and that by chlorobenzene is red. When nitrated in the vapor phase with fuming nitric acid, 1 part of benzene on a weight basis gives a color equivalent to that of 0.125 part of toluene. Hence even if benzene is present in equivalent amounts to toluene, while the results will be less accurate, it will not vitiate the determination from the industrial-hygiene viewpoint.

For more accurate determinations, the amount of benzene can be estimated and a correction can be applied to the color produced in the nitration of the toluene-benzene vapor mixture.

Where interfering yellows and ambers are present, which are attributable to sampling atmospheres containing soot and tars or solvents which give these colors with this test, they may be eliminated by the following procedure. Extract the neutralized solution with 10 ml. of ether Transfer the ether layer to a Nessler comparison tube and allow the ether to evaporate spontaneously. Take up the residue in 9 ml. of butanone, which is the average volume of the butanone extract, and then proceed with the detailed technique.

3. *Xylene*

Xylene, $C_6H_4(CH_3)_2$, dimethylbenzene, commercial xylol, is a mixture of *o*-, *m*-, and *p*-xylene. It is a colorless, mobile liquid. It is used as a solvent for gums and oils and in the manufacture of dyes and other organic substances. The principal component of commercial xylol is the meta isomer. The boiling range is from about 137–140° C.; it has a specific gravity of about 0.86 and a flash point of 29° C. It is inflammable, with its lower limit about 1 and its upper limit about 6–7. It is practically insoluble in water and is miscible with absolute alcohol and with many of the common organic solvents.

Xylene, like toluene, is not considered particularly toxic but here, too, the substance is less dangerous than benzene primarily because it has a lower volatility and therefore is less likely to build up dangerous concentrations under working conditions similar to those of benzene. Exposure to air concentrations greater than 200 parts per million may result in damage similar to that produced by benzene, and this is the recommended maximum allowable concentration.

Detection and Determination

With the Lippman-Pollak reaction,[37] xylene gives an orange color. It gives the sulfuric acid-formaldehyde test (page 525). It may be estimated by adsorption on air-equilibrated activated charcoal, or on silica gel by general the method detailed on page 482. Where xylene is the air contaminant, it may, in the absence of toluene, benzene, ethylbenzene, and chlorobenzene, be estimated by a butanone method similar to that described for toluene, as it forms a deep blue color.

4. *Solvent Naphtha*

Solvent naphtha, sometimes called coal-tar naphtha, is a mixture of liquid aromatic hydrocarbons consisting mainly of xylol, toluol, benzene, ethylbenzene, and some higher hydrocarbons. The light grade boils in the range from 110° to 160° C. and has a specific gravity of 0.865–0.875. The heavier grade, consisting mainly of the higher aromatic hydrocarbons, has a boiling range from about 160–190° C. They should not be confused with petroleum naphtha, which consists of hydrocarbons of the paraffin group.

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[37] Merck Index (5th ed.), 1940.

Solvent naphtha of the light grade is sometimes used as a diluent in lacquers, paints, and varnishes and the like. Both are used as solvents for gums, oils, resins, and pitches.

The toxicity and physiological response of this mixture of aromatic hydrocarbons is clearly the result produced by its components. The solvents with the lower boiling range will be the more toxic. The maximum allowable concentration recommended for this solvent is 200 parts per million parts of air.

The concentration of the vapor of this solvent mixture in air may best be estimated by the general methods for the determination of the concentration of solvent vapors in air. Since solvent naphtha is not a definite substance, no direct method can be given for its determination.

5. *Ethylbenzene*

This substance has been commercially developed for use as an antiknock agent, especially in airplane fuels. It has some small use as a lacquer diluent and in the synthesis of sterols for sterol-type resins. It is a general solvent, particularly for paraffin waxes and for "spotting" in the production of cellulose acetate silks.

Ethylbenzene, $C_6H_5C_2H_5$, is a colorless liquid which possesses a pungent odor and is irritating to the eyes and mucous membranes. The boiling point of the pure compound is 136.5° C. at 776.7 mm. of mercury; its specific gravity is 0.868 at 20/4° C.; its vapor pressure is 15.3 mm. of mercury at 20° C.; and it has a flash point of 20° C. It is stable and resistant to hydrolysis. The vapor is nearly 4 times heavier than air. It has inflammable limits similar to those of xylene. It is practically insoluble in water and is miscible with the common organic solvents.

The commercial product has a boiling range in which 95 per cent comes over between 135.2–136.5° C.; its specific gravity is 0.8599 at 25/15° C.; it has a flash point of 23.3° C.

a. Physiological Response

The acute physiological response of guinea pigs to the vapors of ethylbenzene was studied by Yant, Schrenk, Waite, and Patty.[38] They found that it was not possible at room temperature to obtain concentrations of ethylbenzene vapor high enough to kill guinea pigs in a short time Exposure to 1 per cent by volume for 30–60 minutes produced marked symptoms and was dangerous to life following exposure. Exposure for 60 minutes to a concentration of 0.7 per cent was the maximum amount without the occurrence of death and 0.3 per cent was the maximum concentration for 60-minute exposure without serious symptoms. The maximum concentration for a single exposure of several hours without serious disturbances was 0.1–0.2 per cent.

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[38] W. P. Yant, H. H. Schrenk, C. P. Waite, and F. A. Patty, *U. S. Pub. Health Repts.*, *45*, 1241 (1930).

In the order of occurrence, the symptoms observed were eye and nose irritation, apparent vertigo, static and motor ataxia, apparent unconsciousness, tremors of the extremities, rapid jerky respiration, then shallow respiration, finally slow, gasping respiration, and death. Exposure to a concentration of 1 per cent caused all of these symptoms in 2–3 hours; a concentration of 0.5 per cent caused all the symptoms up to tremors of the extremities after 8 hours; a concentration of 0.2 per cent caused all symptoms up to motor ataxia in 8 hours; and a concentration of 0.1 per cent caused no symptoms other than eye irritation in 8 hours.

The relative toxicity of ethylbenzene appears to be slightly less than gasoline and benzene in the range of high concentrations and practically the same as gasoline and benzene in moderate and low concentrations.

Ethylbenzene vapors are irritating to the eyes and upper respiratory passages in men in concentrations below those causing serious response in guinea pigs. Vertigo also occurs in advance of serious response from a single exposure. Concentrations of vapor which cause injury in 30–60 minutes or less are intolerable to breathe. The generally accepted maximum allowable concentration for an 8-hour exposure is 200 parts of ethylbenzene per million parts of air.

It should be mentioned in connection with the discussion of warning properties that the action of low concentrations of ethylbenzene vapor differs to some extent from the action of low concentrations of the common irritants such as croton aldehyde, allyl alcohol, acrolein, and others. The irritation produced by the latter compounds increases in severity with continued exposure, whereas the irritation produced by low concentrations of ethylbenzene decreases in perceptible severity with continued exposure. In this respect it acts similarly to odorants. The decrease in perceptible odor intensity of these substances is attributed to olfactory fatigue or paralysis. The decrease in perceptible irritation produced by ethylbenzene may be due to local anesthetic action.[38]

b. Detection and Determination

Ethylbenzene may be detected and estimated by the butanone method described for toluene. It gives a green color in this method. It can be estimated by the general method of adsorption on air-equilibrated charcoal or silica gel and determination of the gain in weight from a measured volume of air-vapor mixture.

6. *Cumene*

Cumene, $C_6H_5CH(CH_3)_2$, isopropylbenzene, is a colorless liquid which has a specific gravity of 0.864 at 20/4° C. It boils at 152–153° C. and has a refractive index of 1.4947 at 15° C. The industrial product is usually obtained by the fractionation of petroleum. It is used as a solvent and as a starting material for other organic chemicals.

The toxicology of cumene has been studied.[39] It has been found that the minimum lethal concentration of cumene, which is of the order of 2,000 parts per million (10 mg. per liter), indicates that this substance has a greater acute toxicity than benzene and toluene. Because it has a relatively low volatility, under ordinary conditions of temperature and pressure, the acute industrial hazards should be less difficult to control than similar hazards from benzene and toluene. These investigators found there was no essential difference in the toxicity of pure cumene and that derived from petroleum. They also point out that the slow rate of elimination of this compound suggests that precautions against possible cumulative effects should be considered.

Its concentration in air may be determined by the methods detailed in Chapter XII.

B. OTHER CYCLIC HYDROCARBONS

1. *Cyclohexene*

Cyclohexene, C_6H_{10}, benzenetetrahydride, is a liquid which boils at about 82–84° C. and has a density of 0.809 at 20° C. It is used as a solvent.

The work of Lazarev[40] shows that this substance is a mild narcotic. The recommended maximum allowable concentration is 400 parts of cyclohexene per million parts of air by volume.

Its concentration in air may be estimated by the methods detailed in Chapter XII.

2. *Styrene*

Styrene, $C_6H_5CH{:}CH_2$, styrene monomer, phenethylene, vinylbenzene, is a colorless liquid with an odor resembling amber and rubber solutions.

[39] H. W. Werner, R. C. Dunn, and W. F. von Oettingen, *J. Ind. Hyg. Toxicol.*, *26*, 264 (1944).

[40] N. W. Lazarev, *Arch. exptl. Path. Pharmakol.*, *143*, 223 (1929).

It has a specific gravity of 0.904 at 25° C.; it boils at 144–146° C.; and it has a refractive index of 1.5439 at 25° C. Styrene is used for the manufacture of Buna S rubber and for other industrial purposes.

On the basis of toxicological studies[41] a maximum allowable concentration of 400 parts per million, equivalent to 1.7 mg. per liter at 25° C. and 760 mm. of mercury, was proposed as an American War Standard.[42] Because, however, this concentration has been shown to be irritating under actual working conditions, the recommended maximum allowable concentration is 200 parts of styrene monomer per million parts of air by volume.

Determination

The concentration of styrene in air has been determined by ultraviolet absorption, by infrared absorption, and by a nitration method.[43]

Nitration Method. In this method styrene in air is trapped by use of a bead trap containing carbon tetrachloride. Butadiene, if present, is removed by heating, the styrene is nitrated, the nitro compound is separated, and the color developed is estimated.

Sampling Use a bead-packed absorber similar to Figure 106 or an analogous device immersed in an ice bath. Bubble the air through the bubbler containing 5 ml. of carbon tetrachloride, at a rate of 1 liter per minute or less.

Preparation of Sample. Transfer the carbon tetrachloride solution to a dry 250-ml. glass-stoppered Erlenmeyer flask, using five 2-ml. portions of carbon tetrachloride to wash the absorber. If the sample contains sufficient water so that water can be seen adhering to the sides of the flask, separate the sample from the water by shaking the sample so that the water collects and wets the walls of the flask. Transfer the carbon tertrachloride solution to another dry flask by decantation and wash the first flask with three additional 3-ml. portions of carbon tetrachloride, decanting each washing in turn from the water.

To remove butadiene, which may interfere with the determination, fit the flask with a ₮ 29/42 male joint about 6 inches long, and immerse the flask 1 to 1.5 cm. in a water bath maintained at 80° C. ± 2° for 20 minutes. Remove the flask and cool to room temperature under a cold-water tap.

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[41] H. C. Spencer, D. D. Irish, E. M. Adams, and V. K. Rowe, *J. Ind Hyg. Toxicol., 24,* 295 (1942).

[42] *Am. Standards,* Z37.15–1944.

[43] V. K. Rowe, J. Atchison, E. N. Luce, and E. M. Adams, *J. Ind Hyg. Toxicol., 25,* 348 (1943).

Procedure. Add 2 ml. of a nitrating mixture consisting of equal volumes of concentrated sulfuric acid and freshly boiled concentrated nitric acid and shake vigorously every 2 minutes over a 10-minute period. Add 20 ml. of water to the flask and shake vigorously. Transfer the contents to a 125-ml. separatory funnel. Wash the flask with two 3-ml. portions of water and add the washings to the separatory funnel. Allow the layers to separate, draw off the carbon tetrachloride layer, and discard. Collect any scum at the interface by swirling and discard along with the carbon tetrachloride. Add an additional 15 ml. of water and draw off any residual carbon tetrachloride and scum. Transfer the aqueous layer via the mouth of the separatory funnel to a 50-ml. volumetric flask, wash the separatory funnel with two 3-ml. portions of water, and make to volume. Measure the transmission, using a B 42 filter.

Preparation of Standard. Dissolve 1 g. of monomeric styrene in carbon tetrachloride and dilute to 100 ml. with this solvent. Dilute 25 ml. of this stock solution with carbon tetrachloride to make a volume of 250 ml. One ml. of this dilute solution is equivalent to 1 mg. of styrene. Pipette 1-, 2-, 3-, 4-, and 5-ml. volumes of the dilute standard equivalent to 1 to 5 mg. of styrene into 250-ml. glass-stoppered Erlenmeyer flasks. Make up the total volume of each standard to 15 ml. with carbon tetrachloride. Add 2 ml. of the nitrating solution and proceed with the method as detailed. A blank should be carried through the same operations with the same reagents.

Butanone Method. Styrene may also be estimated by the butanone method. It develops a green color in this reaction.

C. CONDENSED RING HYDROCARBONS

1. Naphthalene

Naphthalene is used fairly widely in industrial processes: for instance, it is used in the manufacture of dyes, naphthols, synthetic resins; the production of phthalic, maleic, and malic acids; and the manufacture of celluloid, lampblack, and smokeless powder. It is used widely as a moth repellent, as a preservative, as a disinfectant, and as an illuminant.

Naphthalene, $C_{10}H_8$, is a white crystalline solid with a characteristic coal tar odor. It melts at 80.2° C.; boils at 217.9° C.; has a specific gravity of 1.152; and a flash point of 86° C. It sublimes at room temperature and is volatile with steam. It is practically insoluble in cold water and is only slightly soluble in hot water. It is soluble in many of the common organic solvents but is not miscible in all proportions with them.

Poisonings have been reported which are attributable to the inhalation of naphthalene fumes and the ingestion of naphthalene itself, but these have occurred through its use in the home as a moth and insect repellent rather than in industrial use.

Inhalation produces the following symptoms: headache, nausea, vomiting, profuse perspiration, optical disturbances, hematuria, and slight edema. Taken internally, naphthalene produces gastric and urinary disturbances.[44]

Detection and Determination

Appreciable quantities of naphthalene can be detected by its characteristic coal tar odor. The naphthalene can be trapped in alcohol, recrystallized from this solvent, and the melting point and picrate obtained. Naphthalene can also be detected and estimated by the general methods for vapors and solvents.

Picrate Method.[45,46] This method is based on the formation of an additive compound of naphthalene with picric acid, which is insoluble in an aqueous solution of picric acid. The vapor is passed through a bubbler containing a standard solution of picric acid and the excess picric acid is estimated by titration. The method is used for estimation of naphthalene in coal gas.

Procedure. Pass the air or gas through an all-glass train of four bubblers. The first bubbler contains 10 per cent citric acid solution to retain any ammonia or other alkaline vapor; the second contains a known volume of 0.05 *N* picric acid, the third contains a lesser volume of the same normality picric acid, and the fourth is used to retain the picric acid spray. No rubber connections may be used in the train or sampling line because of errors resulting from naphthalene absorption. After a known volume of air or gas has passed through the train, disconnect the train and transfer the contents of bubblers 3 and 4 to bubbler 2. Wash bubblers 3 and 4 with a minimum of water and add the washings to bubbler 2.

Stopper the bubbler with an interchangeable or other stopper equipped with a stopcock and tube, if the bubbler is not equipped with a stopcock side arm. Evacuate the absorption device until the naphthalene picrate rises to the surface. Close the stopcock. Immerse the bubbler in boiling water and heat with occasional shaking. Transfer to a volumetric flask with a volume about equal to the volume of the liquid in the bubbler. Make up to the mark with the washings. Shake well. Filter through a dry filter, rejecting the first portions, and then transfer an aliquot portion of the filtrate by means of a pipette to a flask. Titrate with 0.1 *N* sodium hydroxide solution, using lacmoid or phenolphthalein solution. From the titration of the aliquot the concentration of picric acid in the volumetric flask can be determined. This figure subtracted from the known volume and concentration used in the bubblers gives the amount of picric acid used to form the additive compound, $C_{10}H_8$,-$C_6H_2(NO_2)_3OH$. From this result the amount of naphthalene present can be calculated and by division by the volume of air or gas sampled, the amount of naphthalene per unit volume can be ascertained.

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[44] W. D. McNally, *Toxicology*, Industrial Medicine, Chicago, 1937.
[45] H. G. Colman and J. F. Smith, *J. Soc. Chem. Ind.*, *19*, 128 (1900).
[46] H. G. Colman, *Gas J.*, *144*, 231 (1918).

2. *Tetralin and Decalin*

Tetralin, $C_{10}H_{12}$, the commercial name of tetrahydronaphthalene, Decalin, $C_{10}H_{18}$, the commercial name of decahydronaphthalene, and "Tetralin Extra," a mixture of both, are the catalytic hydrogenation products of naphthalene. They are used as solvents for oils, fats, and waxes, and for rubber and resins. These solvents are also used industrially for cleaning and degreasing fabrics and for fat-stain removers and as a substitute for turpentine.

Tetralin is a colorless liquid with a pentrating odor. It boils at 206–207.5° C.; has a specific gravity of 0.971 at 20/4° C.; a refractive index of 1.5434 at 20° C.; and a flash point of 78° C. It is insoluble in water but is miscible with many organic liquids.

Decalin is a mixture of the *cis* and *trans* forms of decahydronaphthalene. It has a boiling range of 189–191° C.; a refractive index of 1.467–1.479 at 20° C.; a specific gravity of 0.890; and a flash point of about 60° C.

Some authorities state that these solvents are nontoxic to human beings although toxic to insects. However, Galewski[47,48] and Arnstein[49] report both dermatitis and systemic poisoning from the use of these solvents.

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[47] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939).

[48] E. Galewski, *Klin. Wochschr., 3,* 1767 (1924).

[49] A. Arnstein, *Wien. klin. Wochschr., 35,* 488 (1922).

a. Detection of Decalin[49a]

Formaldehyde Reaction. Draw air through 50 per cent alcohol solution in an absorption flask to obtain an alcoholic solution of the solvent. To 1 ml. of the test solution, add 1 ml. of 30 per cent aqueous formaldehyde solution and 10 ml. of concentrated hydrochloric acid or 2 ml. of concentrated sulfuric acid. If concentrated hydrochloric acid is used, heat the mixture to boiling but do not boil if sulfuric acid is used. With hydrochloric acid, decalin gives an orange color when 0.05 g. is present. Tetralin gives no color with 0.2 g. With sulfuric acid 0.01 g. of tetralin suffices to give a distinct pink and 0.1 g. of decalin is required to give a yellow.

Furfural Reaction. The furfural reaction is more sensitive for both decalin and tetralin but there is less differentiation in the colors.

To 6 ml. of the alcoholic solution add 2 drops of 2 per cent alcoholic furfural solution. Add 10 ml. of concentrated hydrochloric acid or 2 ml. of concentrated sulfuric acid. In the presence of decalin a yellow or greenish yellow color is produced. With sulfuric acid about 0.001 g. and with hydrochloric acid about 0.005 g. of the hydrocarbon can be detected.

b. Detection and Determination of Tetralin[49a]

Formaldehyde Reaction. Draw air through 50 per cent alcohol to trap the hydrocarbon. Add 1 ml. of a 30 per cent aqueous formaldehyde solution to 1 ml. of the test solution. Add 10 ml. of concentrated hydrochloric acid or 2 ml. of concentrated sulfuric acid and heat only in the case of the addition of hydrochloric acid. Only in higher concentrations is the solution colored a light greenish yellow. With sulfuric acid, dilute solutions of tetralin yield a red-brown. With higher concentrations, a wine red color is produced.

Furfural Reaction. Dilute 1 ml. of the alcoholic test solution with 5 ml. of alcohol and add 2 drops of a 2 per cent alcoholic solution of furfural. Add 2 ml. of concentrated sulfuric acid or 10 ml. of concentrated hydrochloric acid. In the presence of tetralin a blue color is obtained. The reaction is sensitive to 0.001 g. of the hydrocarbon with sulfuric acid and 0.005 g. with hydrochloric acid.

Estimation. Adsorb the tetralin on activated carbon and weigh or extract from the activated carbon with benzene.[49b] After extraction, fractionate using a weighed Soxhlet flask and an appropriate still head. Weigh the solvent residue. Run a blank.

[49a] A. Castiglioni, *Z. anal. Chem.*, *101*, 414 (1935).

[49b] L. Piatti and O. Spreckelsen, *Z. angew. Chem.*, *43*, 308 (1930).

D. TERPENE HYDROCARBONS

Turpentine

Turpentine, or more particularly, oil of turpentine, is used principally as a solvent in paints and varnishes because it mixes readily with the vehicles used in these products and also because it evaporates quickly. It is also used as a diluent in printing inks, as a solvent in various industries such as in the manufacture of sealing wax and shoe polish, and in the rubber, linoleum, and oil-cloth industry.

Oil of turpentine is not a definite chemical substance, for it is a liquid consisting of a mixture of hydrocarbons. American steam-distilled turpentine consists of from 70 to 90 per cent α- and β-pinene, $C_{10}H_{16}$, about 10 per cent dipentene, and small amounts of other hydrocarbons. Turpentine has a characteristic odor and taste which becomes disagreeable on aging. It has a boiling range of 153–175° C.; a specific gravity of 0.861–.876; a refractive index of 1.459–1.470 at 20° C.; and has a lower limit of inflammability of 0.8. It is insoluble in water; soluble in 5 volumes of alcohol; and miscible with organic solvents, for instance, benzene, chloroform, and ether.

Turpentine is an irritant affecting principally the eyes, lungs, and skin. Even very low amounts produce discomfort. Among the symptoms observed in more severe exposure are irritation of the mucous membranes of the eyes, nose, and upper air passages, cough, bronchial inflammation, salivation, headache and vertigo, irritation of the kidneys and bladder, and severe irritation of the skin. Continued inhalation of the vapors may cause chronic nephritis and a predisposition to pneumonia.

Turpentine from any source is a skin irritant and will cause dermatitis if allowed to remain on normal skin some length of time.[50]

Albaugh[51,52] states that 3 mg. per liter of turpentine, which is approximately equivalent to 919 parts per million, causes local symptoms and that 6 mg. per liter, or 1,878 parts per million, will poison healthy men in 1 to 4 hours. The generally accepted maximum allowable concentration for an 8-hour working day is 100 parts per million.

[50] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939).

[51] A. P. Albaugh, *Ohio Pub. Health J.*, *6*, 512 (1915).

[52] L. Greenburg, *U. S. Pub. Health Service, Reprint* 1096 (1926).

Determination[53,54]

Turpentine vapor can be estimated by the general methods detailed for solvent vapors in Chapter XII. A more particular method is the reaction with vanillin. The air containing turpentine vapor is passed through a bubbler or series of bubblers containing alcohol. To an aliquot of this solution a 1 per cent solution of vanillin in concentrated hydrochloric acid is added. A pink coloration appears immediately and soon changes under spontaneous development of heat to blue-green. This is compared with standards prepared from turpentine obtained from the same source as that in the vapor phase. Since turpentine is not a pure substance, this requirement for the preparation of standards must be followed for accurate results.

Procedure. Bubble 30 liters of air in the course of 1 hour through a series of traps containing 50 ml. of 95 per cent alcohol. Transfer the alcoholic test sample to a volumetric flask and make to volume with 95 per cent alcohol. Pipette 5 ml. of the test solution into a colorimeter tube. Add an equal volume of a freshly prepared 1 per cent solution of vanillin in hydrochloric acid (specific gravity 1.19) and allow to stand for 30 minutes. Compare with a series of standards treated the same way.

A series of standards are prepared in advance by dissolving weighed amounts of turpentine in 95 per cent alcohol and diluting to a known volume.

Other vapors that may be contaminating the air of a workroom such as benzene, benzine, acrolein, and carbon monoxide do not, in alcoholic solution, affect the color of the reagent. Acetone and ethyl methyl ketone give a pink coloration which does not turn to blue-green unless the reaction mixture is heated.

Another colorimetric method for the determination and detection of turpentine vapors in air is based on the intensity of color produced by concentrated sulfuric acid.[55] The vapors are bubbled through and absorbed in concentrated sulfuric acid. The mixture is allowed to stand for 1–3 hours to allow for maximum color development. Quantitative results are obtained by comparison with known amounts of turpentine vapor in sulfuric acid. Benzine and benzene do not interfere.

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[53] V. D. Bogatskii and V. A. Biber, *J. Chem. Ind. (Moscow)*, *5*, 645 (1928); *Chem. Abstracts*, *22*, 4840 (1928).

[54] I. Rosenthaler, *Z. anal. Chem.*, *44*, 292 (1905).

[55] P. Andreev and A. Gavrilov, *J. Chem. Inst. (Moscow)*, *5*, 1282 (1928); *J. Ind. Hyg. Abstracts*, *12*, 5 (1930).

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CHAPTER XV

Halogenated Hydrocarbons

The tremendous expansion in the use of refrigerants, air-conditioning apparatus, fumigants, degreasers, dry cleaners, paint removers, fire extinguishers, solvents, extractants, and medicinals has brought about a great increase in the use of halogenated hydrocarbons, for these substances have certain marked advantages for some of these purposes. However, along with these advantages are the life and fire hazards associated with their use.

In the discussion on phosgene, Chapter X, mention was made of the hazard associated with the thermal decomposition of the chlorinated hydrocarbons, with the formation of phosgene, hydrochloric acid, and chlorine. The halogenated hydrocarbons are harmful in varying degrees just like other organic solvents because of their inherent properties and not only because of their thermal-decomposition products.

a. Physiological Effect

In general, the physiological effect of the halogenated hydrocarbons as a class is one of anesthesia and narcosis with damage and injury chiefly to the visceral organs, especially the liver and, in the case of tetrachloroethane, the kidneys.[1] The halogenated hydrocarbons of the benzene group may also be blood poisons, as illustrated by the effect of *o*- and *p*-mononitrochlorobenzene.[2] The chlorinated hydrocarbons, as a class, have a marked effect on the nervous system because they are lipoid solvents. They act as heart depressants and some cause heart fibrillation.[3]

The relative order of the toxicity of the chlorinated hydrocarbons has not been completely clarified, as a result, perhaps, of the different standards by which they were judged. Lehmann's[4] listing based on the toxicity attributable to the vapor phase, termed the monophasic toxicity, and that representing secondary and cumulative effects (attributable to condensation, depending on temperature and humidity), termed diphasic toxicity, shows different orders for both types. Lazarev[5] obtained a different listing based on work done on mice. Other listings are given by Mueller[6] obtained from the physiological response of mice and by Joachimoglu[7] based on the response of fish. An order of toxicity which may be derived from the maximum concentrations permissible for safety in the workshop as given in Table 5, Appendix, pages 760 to 765, is given in Table 26. A comprehensive review of the chlorinated hydrocarbons is given by Oettingen.[8]

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[1] K. B. Lehmann and F. Flury, *Toxikologie und Hygiene der technischen Loesungsmittel,* Springer, Berlin, 1938.

[2] G. V. Ashcroft and A. Renshaw, *J. Ind. Hyg., 8,* 67 (1926).

[3] W. J. McConnell, *J. Am. Med. Assoc., 109,* 762 (1937).

[4] K. B. Lehmann, *Arch. Hyg., 74,* 1 (1911).

TABLE 26

Order of Toxicity of Chlorinated Hydrocarbons[a]

Compound	Ppm.	Mg./l.
Tetrachloroethane	5	0.035
2-Chlorobutadiene	25	0.1
Trichloroethane	50	0.15
o-Dichlorobenzene	50	0.32
Carbon tetrachloride	50	0.35
1,2-Dichloroethane	75	0.33
Monochlorobenzene	75	0.37
Methyl chloride	100	0.22
1,1-Dichloroethane	100	0.43
Chloroform	100	0.53
Tetrachloroethylene	100	0.74
Trichloroethylene	150	0.82
Dichloroethylene	200	0.8
Vinyl chloride	500	1.28
Dichloromethane	500	1.75
Ethyl chloride	1,000	2.88

[a] Based on recommended maximum allowable concentrations. Conversions from ppm. to mg./l. and vice versa are approximate.

b. Classification of Methods Used for Halogenated Hydrocarbons

The methods used for the detection and determination of the halogenated hydrocarbons may be summarized briefly as follows:

Detection
  (1) Flame tests
  (2) Colorimetric tests
Determination
  (1) Adsorption on air-equilibrated activated charcoal and silica gel

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[5] N. W. Lazarev, *Arch. exptl. Path. Pharmakol.*, *141*, 19 (1929).
[6] J. Mueller, *Arch. exptl. Path. Pharmakol.*, *109*, 276 (1925).
[7] G. Joachimoglu, *Biochem. Z.*, *120*, 263 (1923).
[8] W. F. von Oettingen, *J. Ind. Hyg. Toxicol.*, *19*, 349 (1937).

(2) Thermal decomposition with subsequent estimation of the decomposition products
(3) Colorimetric methods
(4) Physical-chemical methods depending on vapor pressure, specific gravity measurements, refractive index measurements, light absorption measurements, and thermal conductivity.

Detection and estimation by flame tests will be discussed under the section concerning methyl bromide, page 601.

Estimation by means of adsorption on charcoal and silica gel has been fully described in Chapter XII.

Methods discussing thermal decomposition with subsequent estimation of the decomposition products will be detailed under the sections covering methyl chloride (page 562) and carbon tetrachloride (page 570).

Colorimetric methods will be described in this chapter, for instance, the methods for the determination of chloroform and trichloroethylene in air.

The physical-chemical method depending upon the vapor pressure exerted by the condensed halogenated hydrocarbons may be briefly described. See also Chapter XII, page 491.

Vapor Pressure Method. Nuckolls[9,10] estimated the concentration of carbon tetrachloride, chloroform, dichloroethylene, dichlorodifluoromethane, dichlorotetrafluoroethane, ethyl bromide, ethyl chloride, methyl bromide, methyl chloride, methylene chloride, and monofluorotrichloromethane, respectively, in air by means of a modified Burrell apparatus, which consisted essentially of a liquefaction bulb having a side arm connected to a mercury manometer. The inlet of the bulb was provided with a three-way stopcock which connected on one side to a vacuum pump and on the other side to a U-tube, one arm of which was provided with a connection to the sampling tubes.

Water vapor is removed by contact with anhydrous magnesium perchlorate and the sample of halogenated hydrocarbons is frozen in the bulb by cooling with liquid oxygen. The air is then removed from the bulb by means of the vacuum pump. The bulb is brought back to its original temperature, the pressure exerted by the vaporized halogenated hydrocarbon is measured by means of the mercury manometer, and the barometric pressure is noted. From these pressure observations the concentration of the halogenated hydrocarbon in the original sample is calculated.

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[9] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).
[10] J. C. Olsen, H. F. Smyth, G. E. Ferguson, and L. Scheflan, *Ind. Eng. Chem., Anal. Ed., 8,* 260 (1936).

Specific-gravity measurements and refractive-index measurements may be made on the isolated chlorinated or halogenated hydrocarbon and the substance may thus be identified from its characteristic constants.

A. CHLORINATED HYDROCARBONS

1. Methyl Chloride

Methyl chloride is chiefly used industrially as a refrigerant. One trademark for this substance is "Artic." Methyl chloride, CH_3Cl, is a colorless gas which may be relatively easily compressed to a colorless liquid with an ethereal odor, and a sweet taste. It boils at —24° C.; has a specific gravity of 1.782 referred to air at standard temperature and pressure; and is moderately flammable. It has a lower limit of inflammability of 8.2 and an upper limit of 18.7. Its general fire hazard is very much less than gasoline.[9,11,12]

a. Physiological Response

Methyl chloride is a dangerous anesthetic and narcotic. With increase in its use as a refrigerant has come a greater frequency of poisoning from this substance. McNally[13] mentions 98 cases which he investigated, some of which were fatal.

Poisoning with commercial methyl chloride gas produces a characteristic clinical picture of which the outstanding symptoms are drowsiness, mental confusion, coma, nausea, vomiting, and, in severe cases, convulsions and death. The temperature, pulse, and respiratory rate are all increased. There is also evidence of primary anemia and decreased blood pressure.[14]

Exposure of guinea pigs to high concentrations of methyl chloride brings about symptoms chiefly of an anesthetic character such as excitement, rapid loss of equilibrium, inability to walk, struggling, and running motion of the legs. With low concentrations of vapor and long exposure, the principal symptoms in guinea pigs were weakness, rapid pulse, convulsive rapid respiration, and, in some cases, frothy exudate from the nostrils. After exposure, the anesthetic effect produced by high concentrations disappeared rapidly, but the symptoms produced by long exposure

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[11] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 1418* (1926).

[12] *Nat. Bd. Fire Underwriters*, List of Inspected Gas, Oil, and Miscellaneous Appliances (1938).

[13] W. D. McNally, *Toxicology*. Industrial Medicine, Chicago, 1937.

[14] A. H. Kegel, W. D. McNally, and A. S. Pope, *J. Am. Med. Assoc.*, *93*, 353 (1929).

to low concentrations, such as weakness and rapid respiration and pulse, increased and death usually ensued later on.[15]

Expressed in terms of concentration, Sayers and his co-workers[15] found that concentrations of 15–30 per cent by volume of methyl chloride kill most animals in a very short time of exposure; a concentration of 2–4 per cent is dangerous after exposure of from 30 to 60 minutes; the maximum concentration tolerated by the guinea pigs for an exposure of 60 minutes without serious disturbances was 0.7 per cent; and the maximum concentration tolerated for several hours without serious disturbances or aftereffect was 0.05–0.1 per cent.

White and Somers[16] found the minimum lethal concentration in air for guinea pigs exposed for 72 hours was 75 parts per million, or 0.0075 per cent. The acute and chronic toxicity of methyl chloride for several animal species is discussed by Smith and von Oettingen.[17]

It will be noted that there is a definitely delayed toxic action in the behavior of methyl chloride with a marked increase in toxicity as the exposure is prolonged. Methyl chloride does not give adequate warning of its presence in air in concentrations harmful to life. It is, however, decomposed by contact with flame or hot surfaces with the formation of toxic fumes containing hydrogen chloride and phosgene, which have adequate warning properties.[18] The generally accepted maximum allowable concentration of methyl chloride in a working atmosphere is 100 parts per million.

b. Detection and Estimation

The presence of methyl chloride in air can be detected by a modified Beilstein test for halides, with the production of a green flame when a flame impinges on a copper strip in the presence of a halide vapor.[19,20]

Samples of vapor-air mixture may be taken by means of mercury displacement and analyzed volumetrically burning the methyl chloride by slow combustion with a white-hot platinum coil and a large excess of oxygen. The combustion is continued until a constant reading is obtained, after which the products of combustion are absorbed in sodium hydroxide solution. The amount of vapor may be calculated from the combustion data.[15] This method is applicable to relatively large concentrations of halide vapor in air.

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[15] R. R. Sayers, W. P. Yant, B. G. Thomas, and L. B. Berger, *U. S. Pub. Health Service, Bull. 185* (1929).

[16] J. L. White and P. P. Somers, *J. Ind. Hyg., 13,* 273 (1931).

[17] W. W. Smith and W. F. von Oettingen, *J. Ind. Hyg. Toxicol., 29,* 47 (1947); *29,* 123 (1947).

[18] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

[19] V. A. Stenger, S. A. Shrader, and A. W. Beshgetoor, *Ind. Eng. Chem., Anal. Ed., 11,* 121 (1939).

[20] W. L. Ruigh, *Ind. Eng. Chem., Anal. Ed., 11,* 250 (1939).

As noted on page 559, Nuckolls used a vapor-pressure method for the estimation of methyl chlorine.

Combustion Method.[21] The following procedure is very similar to the Referees' method for determining total sulfur in fuel gases. The air containing the methyl chloride is mixed with natural gas and burned in a microburner. The halogen products formed by the combustion combine with ammonia obtained from ammonium carbonate cubes placed around the burner, and also with ammonium hydroxide formed by the ammonia from the ammonium carbonate and the water in the products of combustion of the gas. The chlorides produced are collected and estimated by the Volhard method or other suitable method.

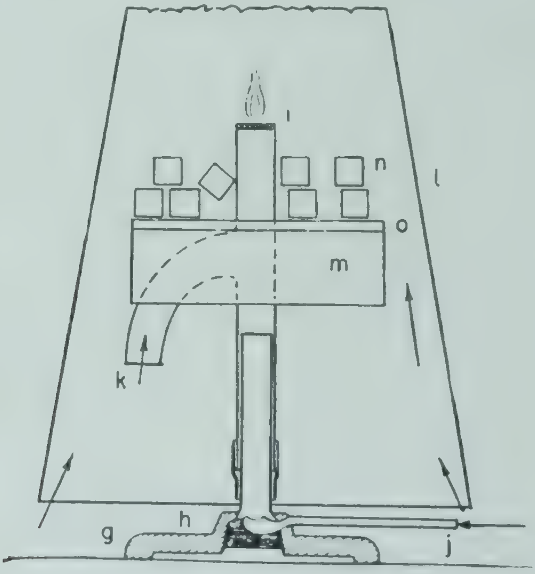

Fig. 110. Micro burner for combustion of methyl chloride.

Apparatus. The apparatus consists of a microburner (Fig. 110), which is constructed by placing a glass T-tube tightly over the burner stem of an ordinary laboratory microburner, *g*, and sealing the primary air intake with wax, *h*. A piece of platinum gauze, *i*, is fused onto the burner tip to stabilize the flame. The connection between the stem and the arm of the T-tube is made gas-tight by means of a rubber-tubing collar.

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[21] F. A. Patty, H. H. Schrenk, and W. P. Yant, *Ind. Eng. Chem., Anal. Ed.*, 4, 259 (1932).

The fuel gas enters at *j* and the methyl chloride-laden air at *k*. Secondary air enters the trumpet tube wall, *l*, and a cork base, *m*, supports the ammonium carbonate cubes, *n*. The cork is covered with a sheet of asbestos, *o*. This cork is smaller than the base of the trumpet tube covering the microburner in order to permit secondary air to be drawn by convection up the rest of the apparatus. The microburner is covered by a trumpet tube, which leads the vapors of combustion and the secondary air into an absorption tower filled with glass beads, under which is placed a beaker to collect the condensate. A Cottrell electrical precipitator is attached to the upper end of the absorption tower to precipitate any halides in the effluent gas stream.

Procedure. The methyl chloride-air sample confined in a microburette is forced into a stream of air by opening the stopcock at the top of the burette and slowly displacing with mercury. The air used to dilute the sample is measured and the rate controlled by means of a dry meter. The mixture is led through glass tubing to the microburner. All connections are glass-to-glass held in place by rubber tubing. The time of burning depends on the quantity of methyl chloride. Blank determinations should be made on room air. Patty and co-workers found that they obtained an average blank titration of 0.05 ml. of 0.025 *N* silver nitrate solution, which is equivalent to 0.07 mg. of methyl chloride.

Wash the chlorides from the trumpet tube, the Cottrell precipitator, and the absorption tower until the washings give a negative test for chlorides. This is best accomplished in the tower by quickly pouring four or five 50-ml. portions of water over the beads. Add the washings to the condensate which collected and dropped from the tower during the combustion. Estimate the chlorides by the Volhard method (page 380), using an excess of 0.025 *N* standard silver nitrate solution and back-titration with standard potassium thiocyanate solution, and using ferric alum as the indicator. The precipitated silver chloride may be removed by filtration prior to titration with the thiocyanate solution. One ml. of 0.025 *N* silver nitrate solution is equivalent to 1.4 mg. of methyl chloride. This method is adequate for methyl chloride concentrations of the order of 50 parts per million.

An alternative combustion method for the determination of methyl chloride in air depending on the decomposition of methyl chloride by an electric spark has been proposed.[22] In this method a measured volume of air is passed through an electric spark between carbon electrodes. The products of combustion are absorbed in sodium arsenite solution. The latter is acidified slightly with nitric acid and silver nitrate is added. The turbidity produced, attributable to silver chloride, is estimated by comparison with standards in Nessler tubes.

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[22] J. L. Franklin, E. L. Dunn, and R. L. Martin, *Ind. Eng. Chem., Anal. Ed., 18,* 314 (1946).

2. Dichloromethane (Methylene Chloride)

Dichloromethane, methylene chloride, CH_2Cl_2, is a solvent for cellulose acetate, fats, oils, and rubber. It is used commercially for degreasing, in cleaning fluids, in paint removers, and in the artificial silk industry as a "stretching" solvent. Dichloromethane is a colorless liquid which boils at 40–41° C.; has a specific gravity of 1.335 at 15/4° C.; has a refractive index of 1.3348 at 15° C.; its vapor is not inflammable and will not form explosive mixtures with air at ordinary temperatures. It is, however, decomposed by contact with a flame or with very hot surfaces with the formation of toxic fumes, and will form weakly combustible mixtures with air at higher temperatures. About 2 g. are soluble in 100 ml. of water and it is miscible with alcohol and ether.

a. Physiological Response

Methylene chloride is anesthetic and narcotic in action; it was used in Germany under the name of "Solaesthin" as an anesthetic and is used for local anesthesia at times. Nuckolls[23] studied the effect of methylene chloride on guinea pigs. He found that exposure of guinea pigs to the vapors of methylene chloride in concentrations of the order of $2^1/_2$ per cent by volume for durations of the order of 2 hours was not lethal. Concentrations of the order of 5 per cent by volume for durations of exposure of $^1/_2$ hour were lethal to guinea pigs. Methylene chloride appears to be less toxic than methyl chloride, dichloroethylene, ethyl bromide, and other halogenated hydrocarbons. While repeated 7-hour exposures, 5 days a week for 6 months, to 5,000 parts per million (17 mg./l.) to dichloromethane was tolerated by rats, dogs, and rabbits, though guinea pigs were adversely affected[24] the running activity of male rats was greately diminished.[25] The recommended maximum allowable concentration is 500 parts per million.

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[23] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard,* 2375 (1933).

[24] L. A. Heppel, P. A. Neal, T. L. Perrin, M. L. Orr, and V. T. Porterfield, *J. Ind. Hyg. Toxicol., 26,* 8 (1944).

[25] L. A. Heppel and P. A. Neal, *J. Ind. Hyg. Toxicol., 26,* 17 (1944).

b. Determination

The concentration of methylene chloride vapor in air can be determined by the vapor-pressure or thermal-decomposition methods detailed in this chapter or by the general-adsorption methods given in Chapter XII.

3. Chloroform

Chloroform, trichloromethane, $CHCl_3$, is used commercially as a solvent in lacquers and as a solvent for fats, oils, rubber, alkaloids, rubber, waxes, and resins. It is used in the manufacture of artificial silk, in the formulation of floor polishes, in the rubber industry, and as a cleaning fluid.

It is a colorless liquid with a characteristic odor and a sweet taste. It boils at 61–62° C.; has a specific gravity of 1.484 at 20/20° C.; and a refractive index of 1.4476 at 20° C. One ml. of chloroform dissolves in about 200 ml. of water. It is miscible with alcohol, benzene, ether, petroleum ether, and other organic solvents. Chloroform is a noninflammable and nonexplosive substance at ordinary temperatures but at higher temperatures under favorable conditions it is capable of forming weakly combustible mixtures with air. It can be decomposed into toxic substances by a flame or other source of high temperatures.

a. Physiological Response

Chloroform is a well-known anesthetic. Symptoms caused by the inhalation of the fumes are, in the initial stage, a feeling of warmth of the face and body, then an irritation of the mucous membranes and skin, followed by nervous aberration. After this period of excitation there is a loss of reflexes followed by shallow respiration and unconsciousness. Prolonged inhalation will bring on paraylsis accompanied by cardiac and respiratory failure and finally death.

Concentrations of 6.8 to 8.2 per cent by volume of chloroform vapor in air will kill most animals in a few minutes. A concentration of 1.4 per cent by volume is dangerous to life after exposure of from 30 to 60 minutes. The maximum concentration tolerated by animals for durations of exposure of 60 minutes without serious disturbances is 0.5–0.6 per cent. The maximum concentration tolerated for several hours or for prolonged exposure with but slight symptoms is 0.2 per cent.[26]

Chloroform is lethal to guinea pigs in concentrations of the order of 2–2.5 per cent by volume for durations of exposure of the order of 1 hour.

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[26] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem., 26,* 1251 (1934).

Nuckolls[27] points out that the difference between the concentrations of chloroform which may be tolerated when breathed continuously for an hour or two and those which are lethal is apparently small.

Flury states that concentrations of chloroform of 25,000 parts per million (2.5 per cent) are lethal to man in 5–10 minutes; 15,000 parts per million (1.5 per cent) are dangerous in 30 to 60 minutes; and 5,000 parts per million (0.5 per cent) can be tolerated for 30 to 60 minutes. The generally accepted maximum allowable concentration is 100 parts of chloroform per million parts of air by volume.

b. Detection and Determination

Chloroform vapor in air can be estimated by the general method for solvents and by the combustion method described for carbon tetrachloride. It can be detected by trapping the vapor in an efficient bubbler using water or alcohol as the trapping agent, and then applying the well-known phenylisocyanide, or carbylamine, reaction.

Carbylamine Reaction. To an aliquot portion of the sample in a test tube, add 1 drop of aniline and 1–2 ml. of alcoholic potassium hydroxide solution, shake, and heat gently. The presence of chloroform is indicated by the offensive odor of phenylisocyanide. This reaction is not specific and will be given by chloral hydrate, iodoform, bromoform, and trichloroacetic acid.

Colorimetric Method. When a solution containing chloroform is treated with pyridine and sodium hydroxide solution and is heated in a water bath for 1 minute, a pink color develops.[28-31] The color produced in this manner may be estimated against similarly treated chloroform standards, against permanent colored-glass standards, or against artificial standards prepared from basic fuchsin.

Trap the chloroform vapor in an efficient bubbler containing either 0.01 per cent hydrochloric acid solution or 95 per cent alcohol, or a 70 per cent aqueous alcohol solution containing 1 per cent tartaric acid. Transfer to a volumetric flask and make to volume.

Procedure. Pipette 10 ml. of 20 per cent sodium hydroxide solution into a tall-form 50-ml. test tube. Add 5 ml. of colorless pyridine by means of a pipette and then transfer an accurate 5-ml. aliquot of the test solution to these reagents. Mix and stopper loosely to prevent undue evaporation of the pyridine. Immerse the tubes in a boiling-water bath so that the reaction mixture is covered by the boiling water and heat for 1 minute. Cool rapidly in running water or ice to 20° C. and allow the layers to separate. Transfer the supernatant pyridine layer by means of a pipette or burette used as a separatory funnel to a color-comparison tube and compare with color standards treated the same way at the same time.

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[27] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

[28] K. Fujiwara, *Sitzber. Abhandl. naturforsh. Ges. Rostock, 6,* 1 (1914); *Chem. Abstracts, 11,* 3201 (1917).

[29] W. H. Cole, *J. Biol. Chem., 71,* 173 (1926).

[30] A. O. Gettler and H. Blume, *Arch. Path., 11,* 555 (1931).

[31] J. H. Ross, *J. Biol. Chem., 58,* 641 (1923–4).

Standards. To prepare a 0.1 per cent stock solution, dissolve 1 g. of chloroform in water and dilute to 1 liter. If desired, 5 ml. of concentrated hydrochloric acid may be added to the chloroform solution before making to volume. Each ml. of this solution is equivalent to 1 mg. of chloroform. Preserve in glass-stoppered bottles.

Permanent standards can be made from a nearly saturated solution of basic fuchsin in acidified alcohol. This stock solution is diluted until it matches as closely as possible the colors obtained from known concentrations of chloroform. These permanent standards should be restandardized frequently. The dye solution does not match the color produced by lower concentrations of chloroform exactly.

This reaction is given by other trihalide-carbon linkages such as bromoform, iodoform, chloretone, chloral, etc.

Nicloux's Method. The chloroform is hydrolyzed by the use of a solution of potassium hydroxide in alcohol. The resultant chloride ion is estimated by direct titration with standard silver nitrate solution, using potassium chromate as the indicator.

Transfer the sample trapped in alcohol to an Erlenmeyer flask. Dilute to 60 ml. and add 10 ml. of 10 per cent chloride-free alcoholic potassium hydroxide solution. Attach to an efficient reflux condenser and boil gently for 30–60 minutes. Cool, wash the condenser with two 10-ml. portions of water, remove the flask from the condenser, neutralize to phenolphthalein indicator solution with dilute sulfuric acid and titrate with standard silver nitrate solution, using 0.5 ml. of a 5 per cent neutral potassium chromate solution as indicator. The use of a porcelain casserole for the titration aids in defining the end point.

The use of a silver nitrate solution containing 8.535 g. per liter simplifies calculations, for 1 ml. of this solution is equivalent to 2 mg. of chloroform.

Fajans Method. The use of dyes which are adsorbed near the end point of a titration has been investigated by Fajans[32] and by Kolthoff.[32a] Dichlorofluorescein is adequate for dilute chloride solution and concentrations of the order of 0.0005 *N* in chloride ion may be titrated with an accuracy of 1 to 2 per cent.

Indicator Solution. Prepare a 0.1 per cent solution of dichlorofluorescein in 60–70 per cent alcohol or a 0.1 per cent solution of the sodium salt of the dye in water. About 2.5 ml. of 0.1 *N* sodium hydroxide solution are required to neutralize 100 mg. of the indicator.

Procedure. Add 2–4 drops of indicator solution to 50 ml. of the test solution and titrate with standard silver nitrate solution. As the end point is reached the silver chloride flocculates. Near the end point the solution turns brown; when the end point is reached the color changes sharply to orange. A slight excess of silver nitrate produces a rose or red color.

4. Carbon Tetrachloride

This chlorinated solvent is used as a degreaser for metal parts, as a cleaning agent in dry cleaning, in the extraction of fats, as a solvent for crude rubber, lac, resins, etc.; in the vulcanization of rubber, in fire extinguishers, as a component of insecticide sprays and soap solution, as a delousing agent, as a dry hair shampoo, and as an anthelmintic drug, for it is almost specific against hookworm.[33] As a fire extinguisher, it is a component of a product sold under the trade mark "Pyrene" and as a dry cleaining agent it is sold under many trade names, one of which is "Carbona." "Chlorasol" is a trade mark for a mixture of 25 per cent carbon tetrachloride and 75 per cent ethylene dichloride and is used as a fumigant.

Carbon tetrachloride, tetrachloromethane, CCl_4, is a colorless, noninflammable liquid with a characteristic odor. It boils at 76.7° C.; has a specific gravity of 1.589 at 25° C.; and has a refractive index of 1.4607 at 20° C. One ml. of carbon tetrachloride is soluble in about 2,000 ml. of water. It is miscible in all proportions with alcohol, benzene, chloroform, ether, petroleum ether, and similar organic solvents. While carbon tetrachloride is noninflammable at ordinary temperatures, at elevated temperatures it will decompose with the formation of small quantities of hydrochloric acid and phosgene. Under ordinary conditions, when carbon tetrachloride is used to extinguish fires in relatively open spaces the concentrations of phosgene and hydrochloric acid produced are irritating but not very harmful, but in small enclosed spaces, such as in a vault, a closet, or a small cellar room, especially where there is no simple exit, there is danger of sufficiently high concentrations of these toxic substances to be harmful.[34] The decomposition products of carbon tetrachloride have adequate lachrymatory warning properties.

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[32] K. Fajans and H. Wolff, *Z. anorg. allgem. Chem.*, *137*, 221 (1924).

[32a] I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis. Titration Methods*, Interscience, New York, 1947.

[33] K. O. Møller, *J. Ind. Hyg.*, *15*, 418 (1933).

a. Physiological Response

Carbon tetrachloride is an anesthetic. The symptoms caused by carbon tetrachloride poisoning are irritation of the nose, eyes, and throat, headache, nausea, vomiting, abdominal pain, diarrhea, stupor deepening into coma, convulsions, weak pulse, fever, uremia, and death. The safety limit for prevention of acute poisoning is given as 1,000 parts per million by the U. S. National Safety Council. The Retail Credit Co.[35] of Atlanta, Ga., regards the safety limit for acute intoxication as ranging from 1,000–1,600 parts per million. The safe limit for continuous exposure is regarded as 100 parts per million by Davis[36] and also by Smyth, Smyth, and Carpenter.[37] The maximum allowable concentration recommended by the American Conference of Governmental Industrial Hygienists[37a] is, however, only 50 parts per million.

Carbon tetrachloride is lethal to guinea pigs in concentrations of the order of 2–2.5 per cent by volume for continuous durations of exposure of the order of 1 hour.[34] A concentration of 4.8–6.3 per cent by volume of carbon tetrachloride vapor in air will kill most animals in a few minutes. Concentrations of 2.4 to 3.2 per cent by volume are dangerous to the life of animals for durations of exposure of from 30 to 60 minutes. The maximum concentration tolerated for 60 minutes without serious disturbances is in the range 0.4–0.6 per cent and the maximum concentration tolerated for several hours or for prolonged exposure with but slight symptoms is 0.16 per cent.

The least detectable odor of carbon tetrachloride vapor in air is 71.8 parts per million.[38,39]

[34] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).
[35] *J. Am. Med. Assoc., 97,* 48 (1931).
[36] P. A. Davis, *J. Am. Med. Assoc., 103,* 962 (1934).
[37] H. F. Smyth, H. F. Smyth, Jr., and C. P. Carpenter, *J. Ind. Hyg. Toxicol., 18,* 277 (1936).
[37a] *Ind. Hyg. Newsletter, 7,* No. 8, 15 (1947).
[38] R. R. Sayers, W. P. Yant, B. G. H. Thomas, and L. B. Berger, *U. S. Pub. Health Service, Bull. 185* (1929).
[39] R. R. Sayers, J. M. DallaValle, and W. P. Yant, *Ind. Eng. Chem., 26, 1251* (1934).

Carbon tetrachloride is about twice as toxic as chloroform, which itself is about 100 times as toxic as ethyl alcohol.[40] McConnell[41] states that carbon tetrachloride is more toxic than chloroform. Its narcotic effects are less marked but its effect on the liver, heart, and kidneys is much more rapid.

b. Detection and Determination

Carbon tetrachloride gives the flame reactions of the organic halogen compounds and imparts a greenish color to the flame. It gives the phenylisocyanide reaction but does not give the naphthol or resorcin tests given by chloroform. A drop of liquid tetrachloride can be used to distinguish it from chloroform. Place the drop in a test tube. Stopper the tube loosely and heat gently. Carbon tetrachloride will decompose, yielding substances that give the starch-iodide test. Chloroform does not give this reaction. Carbon tetrachloride does not reduce Fehling's solution whereas chloroform does.[42]

Carbon tetrachloride vapor may be estimated by the general methods for solvent vapors detailed in Chapter XII, and by the vapor-pressure method described on page 559. The concentration of its vapor in air may also be ascertained by physical methods such as the use of an interference refractometer as described by Smyth, Smyth, and Carpenter.[43] More generally carbon tetrachloride vapors are estimated by combustion methods. The following procedure is a variation of these methods.

Combustion Method. The method is based on the principle that the vapor of chlorinated hydrocarbons mixed with moist air is decomposed quantitatively into hydrogen chloride when passed through a silica tube heated to 1000–1100° C.,[44,45] or at 850° C. if catalyzed by platinum foil.[45a] By absorption and estimation of the hydrogen chloride formed, the concentration of chlorinated hydrocarbon in air may be calculated. If water vapor is not present in sufficient amount, small amounts of chlorine are produced. Alford[46] recommends use of a gas-heated, 2-mm.

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[40] A. D. Waller, *Lancet, 1909,* II, 369.

[41] W. J. McConnell, *J. Am. Med. Assoc., 109,* 762 (1937).

[42] N. Schoorl, *Pharm. Weekblad, 72,* 751 (1935).

[43] H. F. Smyth, H. F. Smyth, Jr., and C. P. Carpenter, *J. Ind. Hyg. Toxicol., 18,* 277 (1936).

[44] J. C. Olsen, H. F. Smyth, G. E. Ferguson, and L. Scheflan, *Ind. Eng. Chem., Anal. Ed., 8,* 260 (1936).

[45] H. F. Smyth, *Ind, Eng. Chem., Anal. Ed., 8,* 379 (1936).

[45a] B. D. Tebbens, *J. Ind. Hyg. Toxicol., 19,* 204 (1937).

[46] W. C. Alford, *J. Ind. Hyg. Toxicol., 29,* 396 1947).

by 30-cm. platinum tube for the combustion instead of a quartz tube.

Apparatus. The following apparatus designed by Tebbens is adaptable for field use. The apparatus is mounted on two panels of masonite, each $^1/_8$ inch thick and 12 by 16 inches in surface area. This material is a good electrical insulator when dry. The panels are hinged together in back so that the apparatus can stand without further support on a flat surface or can be clamped flat on an easel for field use. The apparatus may also be mounted in a box (Fig. 111).[46a] Other models are commercially available. Other devices are described by VanFarowe and McClintock[46b] and by Frazier.[46c] The latter device makes use of a furnace heated by burning methyl alcohol and is suitable for sampling in locations where electricity is not available.

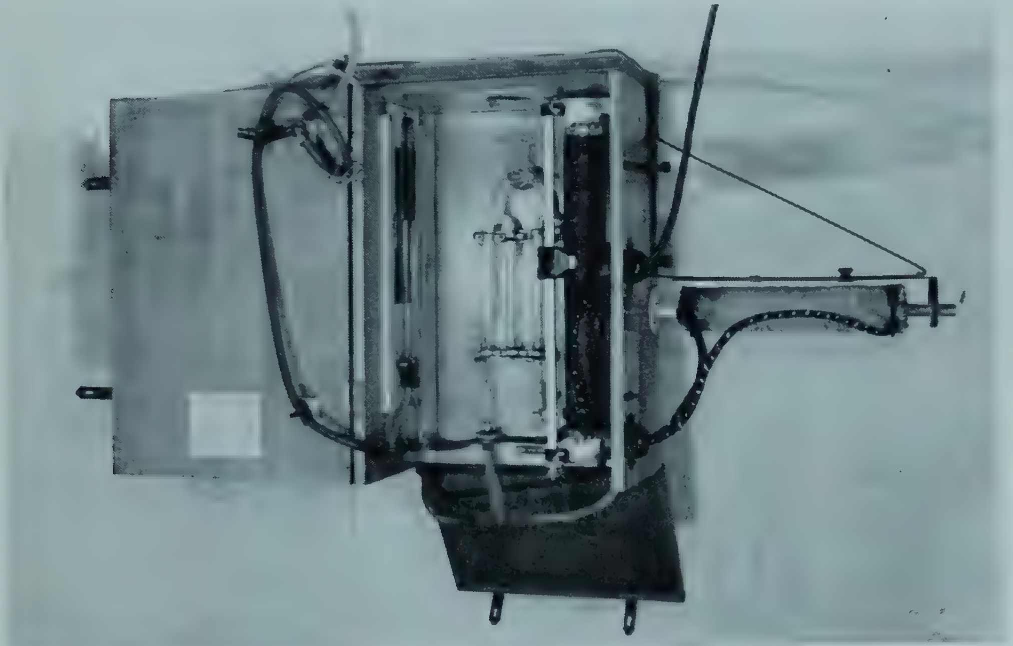

Fig. 111. Combustion apparatus for the determination of halogenated hydrocarbons. (*Courtesy Div. Ind. Hyg. N. Y. State Dept. Labor*)

A silica tube, 15 inches long by $^3/_8$ inch inside diameter, is ground at one end to fit into a No. 9 Ŧ Pyrex joint. It contains 10 square inches of 0.001-inch-thickness platinum foil cut into five strips and fluted to baffle the air as it passes through. The platinum is held in place with asbestos plugs. The platinum both catalyzes the decomposition and provides an increase in contact surface. Combustion temperature is held at 850° C.

[46a] S. Moskowitz and W. J. Burke, *N. Y. State Ind. Bull. 19,* 232 (1940).
[46b] D. E. VanFarowe and R. S. McClintock, *Ind. Hyg. Newsletter, 8,* No. 7, 11 (1948).
[46c] R. Frazier, *Ind. Hyg. Newsletter, 9,* No. 1, 14 (1949).

The furnace consists of 15 feet of No. 22 chromel wire, having a resistance of about 1 ohm per foot, wound on two layers of sheet asbestos around a 10-inch length of the silica tube. Additional layers of asbestos cover the wire to a total diameter of 2 inches. The surface is sufficiently loose to be slipped off the silica tube. It is connected in series with a rheostat having a resistance range from about 16 ohms to zero, and an electrical wall receptacle to which 110-volt electrical power, either alternating or direct current can be plugged in for heating the furnace. The rheostat consists of 16 feet of No. 22 chromel wire wound on a 1-inch asbestos core and tapped at intervals of about 2 ohms.

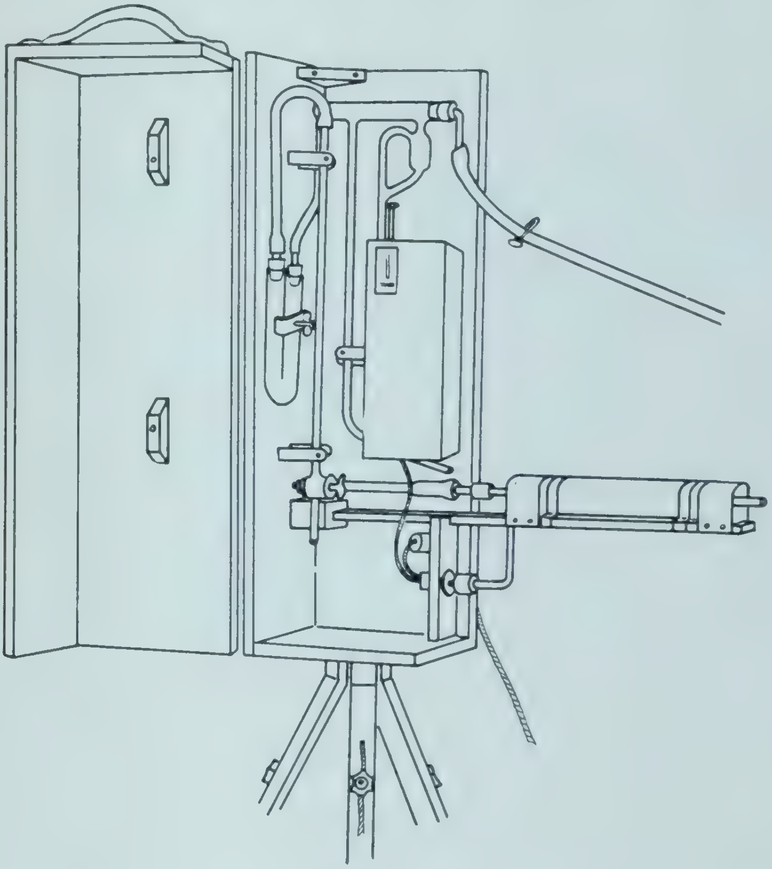

Fig. 112. Combustion analyzer on tripod.

Battery clips are used for the breakable electric connections. The furnace is cradled on angle irons attached to a wooden support, which is held to the rear of the left-hand panel by angle clamps. Both furnace and support may be unmounted for packing. An absorption unit and a flowmeter complete the panel equipment. It is advantageous to place a calcium chloride drying tube between the absorption unit and the flowmeter to prevent condensation of water in the latter.

The absorption unit (Fig. 113) is designed to be filled, emptied, and washed without being removed from the panel. The unit is constructed of Pyrex tubing of 10 mm. inside diameter except for the draining tubes, which are 6-mm. bore. In Figure 113, connection *A* houses the silica tube, *B* is a ground stopper, and *C* is an open tube attached to the flowmeter by means of rubber tubing. The connections and stopper *A*, *B*, and *C* are Pyrex No. 9 ₮ connections.

Glass beads, 2 mm. in diameter, are placed in the upstream side of both legs to a height of about 4 inches and in the draining tubes. They are held in place with glass wool. A small amount of petrolatum is used to lubricate the stopcock, *D*, which is a 3-way stopcock of 4 mm. bore for draining. The other connections are not lubricated. When the silica tube and furnace are removed from connection *A* the unit may be used for other absorptions provided the subsequent reaction or solution in the absorbing medium is fairy rapid. In this way acid or ammonia vapors may be trapped and estimated.

Procedure. After the combustion furnace and silica tube are set in place and connected electrically, run 3 ml. of a saturated solution of sodium carbonate containing 0.5 g. of arsenious oxide per 100 ml. of solution down through *B* and *C* with the stopcock open so that the two legs get equal distribution. This procedure wets the beads and brings the liquid level up to the bottom of the curve of both legs. Turn the stopcock to close all openings and set the cap and tube to the flowmeter in place. Connect the other side of the flowmeter to the inlet side of a vacuum-sweeper centrifugal blower or other adequate sampling device. Bring the heat of the furnace to proper temperature in about 5 minutes by decreasing the resistance of the rheostat to about half. When the silica tube has reached a medium red heat, add the full resistance and draw air through the apparatus at the rate of 1 liter per minute for 5 to 30 minutes, depending on the character of the sample and the concentration encountered.

The air to be tested must be adequately moistened. This moistening is accomplished by soaking a short strip of absorbent cotton with water and placing it in the inlet end of the silica tube so that the heat of the furnace slowly evaporates the water. The cotton wad fills about one-quarter of the cross section of the tube. By leaving a tail of it emerging from the tube, it may be remoistened from time to time. In order to prevent the condensation of this moisture in the fore part of the absorption unit, the furnace is placed about 4 inches from the first bend in the unit.

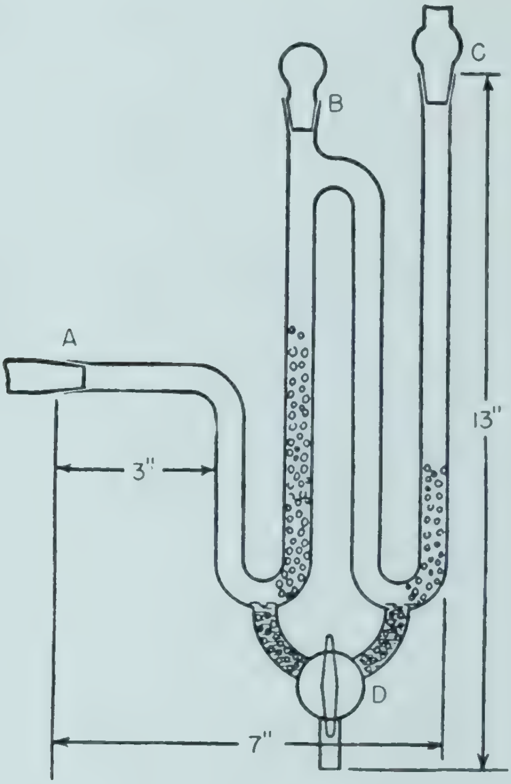

Fig. 113. Absorption unit.[45a]

After sampling is complete wash out the contents of the absorber into a 30-ml. sample bottle placed under the stopcock outlet. Turn the stopcock to connect each leg in turn to the outlet and then wash each one separately with three 2-ml. portions of water. After each washing blow out the wash water by means of the rubber tubing that connects the flowmeter or preferably use an aspirator. With the stopcock closed fill each leg $^1/_2$ inch above the curve and, by blowing gently, rinse the left-hand side of the legs. Do this twice and finally blow out each leg. A total sample of about 25 ml. is obtained. The apparatus is then ready for another determination.

Neutralize the samples, make acid with nitric acid, and titrate by the

Volhard or Mohr method, using 0.03 N solutions. For very low concentrations the amount of chloride may be estimated nephelometrically.

Dudley Combustion Device. Difficulty has been encountered in obtaining complete recovery of halogen from halogenated hydrocarbons. The Dudley device[47,47a] is designed to overcome these difficulties.

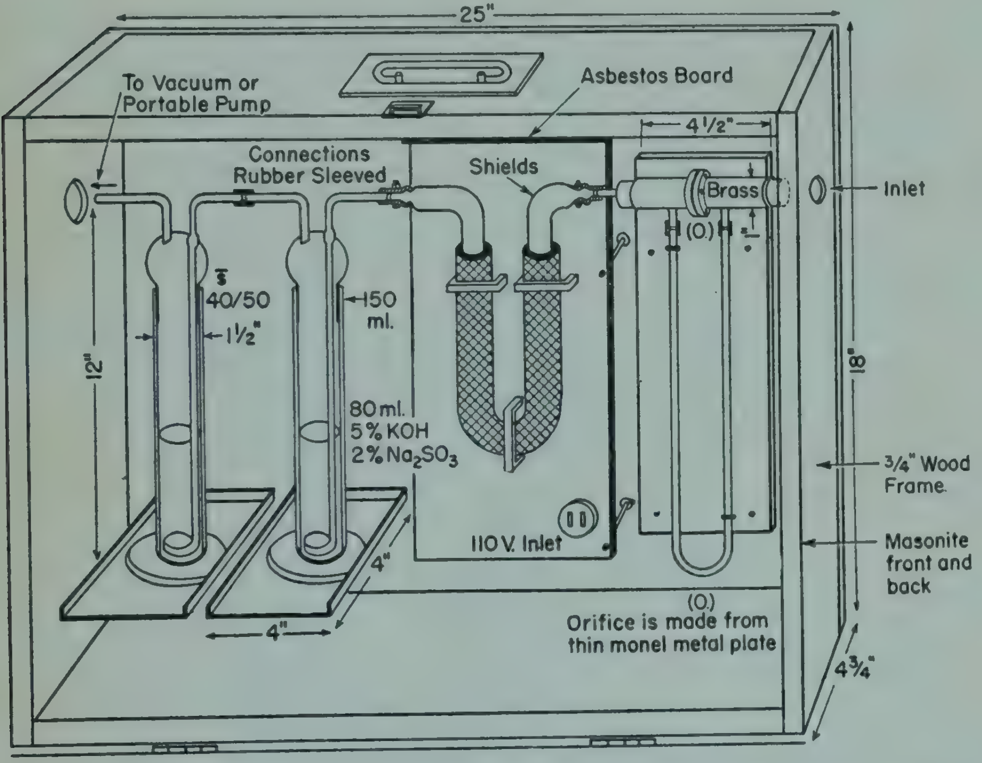
25"
To Vacuum or Portable Pump
Asbestos Board
4 1/2"
Connections Rubber Sleeved
Shields
Brass
(O)
Inlet
40/50
1½"
150 ml.
12"
18"
80 ml. 5% KOH 2% Na₂SO₃
3/4" Wood Frame
110 V. Inlet
Masonite front and back
4"
4"
(O) Orifice is made from thin monel metal plate
4¾"

Fig. 114. Portable unit for sampling atmospheres contaminated with halogenated hydrocarbons.[47]

The sampling apparatus (Fig. 114) consists of a calibrated flowmeter with a thin disk orifice, a one-piece, U-shaped quartz tube containing platinum gauze or coils and heated by an external electrical resistance, and two bubblers, connected in series. A flow of approximately 2.5 liters per minute, provided by vacuum or a motor-driven pump, is convenient. Sampling should be continued for 30 minutes for low concentrations of halogenated hydrocarbon but 5 to 10 minutes sampling time is adequate for obtaining the concentration of methyl bromide in fumigation vaults or chambers and in greenhouses.

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[47] H. C. Dudley, *U. S. Pub. Health Repts.*, *56*, 1021 (1941).
[47a] F. H. Goldman and C. G. Seegmiller, *J. Ind. Hyg. Toxicol.*, *25*, 181 (1943).

The heating element surrounding the quartz tube (Fig. 115) can be made from Nichrome wire by adjusting the length and size of the wire so that a temperature of about 800° C. is obtained. At 110 volts alternating current, the heating elements draw approximately 4 amperes when 35 feet of Nichrome IV, 0.0254 (B. & S. 0.22) wire are used in the winding.

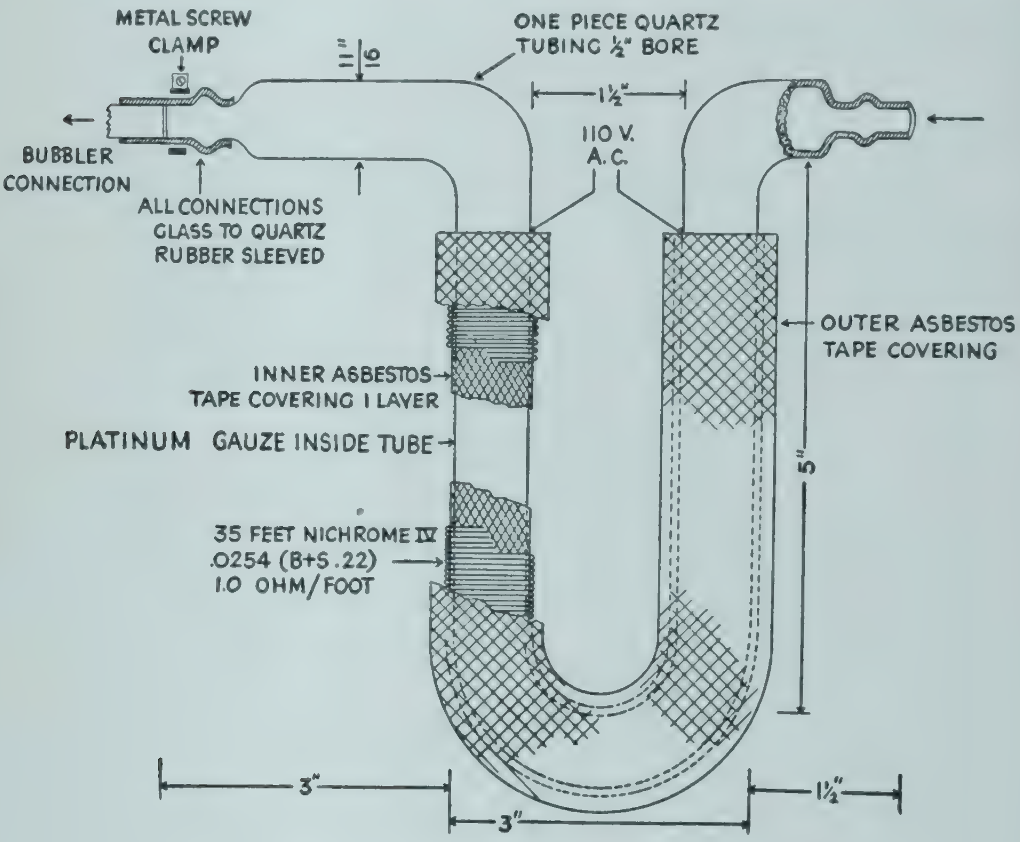
METAL SCREW CLAMP
1/16"
ONE PIECE QUARTZ TUBING ½" BORE
1½"
110 V. A.C.
BUBBLER CONNECTION
ALL CONNECTIONS GLASS TO QUARTZ RUBBER SLEEVED
OUTER ASBESTOS TAPE COVERING
INNER ASBESTOS TAPE COVERING 1 LAYER
PLATINUM GAUZE INSIDE TUBE
5"
35 FEET NICHROME IV
.0254 (B+S .22)
1.0 OHM/FOOT
3"
3"
1½"

Fig. 115. Details of combustion-tube assembly.

Procedure. Place 80 ml. of an aqueous solution consisting of 5 per cent of potassium hydroxide and 2 per cent of sodium sulfite into each bubbler. Sample as directed above. Remove the bubblers from the case, pour the contents into separate flasks, and rinse the bubblers, adding the rinse to the proper flask. Analyze the flasks separately. Make each solution acid with 12 *N* sulfuric acid and add potassium permanganate solution dropwise until excess sulfite has been exhausted. Avoid an excess of permanganate solution. Determine halogen by the Volhard procedure. The sulfite is used to convert any of compounds of the type of phosgene that may be formed to the simple halogen acid.

Recovery of carbon tetrachloride and trichloroethylene is quantitative.

Absorption-Hydrolysis Method. In this method,[47b] carbon tetrachloride or other halogenated hydrocarbon is adsorbed on chloride-free silica, eluted with ethyl alcohol, hydrolyzed with potassium hydroxide, and subsequently estimated titrimetrically by the Mohr method. Recovery of 91 to 99 per cent is obtained.

Sampling. Pass the air to be tested at a rate of 1 liter per minute through two U-tubes containing 7 to 8 g. of magnesium perchlorate and silica gel, respectively. The silica gel should be washed with alcohol and water and heated overnight at 115–120° C.

Procedure. Add the silica gel slowly to 20 ml. of 95 per cent ethyl alcohol kept cool by rotating in a cold-water bath. Allow to stand for 20 minutes at room temperature with occasional shaking. Transfer an aliquot portion to a small glass-stoppered Pyrex bottle and add sufficient chloride-free potassium hydroxide pellets to exceed the amount soluble in the volume of ethyl alcohol chosen. Keep the stopper and inside of the flask neck dry, and hold the stopper in place by means of elastic adhesive tape. Heat the mixture overnight at 50° C. by immersion in a constant-temperature water bath. Neutralize the contents of the bottle with acetic acid using phenolphthalein as indicator, filter, and determine the chloride titrimetrically with silver nitrate and potassium chromate or with silver nitrate and an adsorption indicator (page 567).

Differentiation from Dichloromethane and Trichloroethylene. Carbon tetrachloride can be differentiated from trichloroethylene and dichloromethane by a series of color reactions.[47c]

Adsorb the vapors from the atmosphere being tested on activated charcoal. Drive off the chlorinated hydrocarbons by means of steam distillation, and separate the chlorinated hydrocarbons from the aqueous portion of the distillate.

To one drop of the chlorinated hydrocarbon, add 2 ml. of a 2 per cent solution of α-naphthol in cyclohexanol (I) or 2 ml. of cyclopentanol (II) and a pellet of sodium hydroxide. Heat to boiling and continue heating for 25 seconds. Transfer to another test tube and cool. Note the color and underlay with an equal volume of 85 per cent sulfuric acid or with glacial acetic acid. Allow to stand 1 minute and shake. Compare with the colors noted in Table 26A.

[47b] L. V. Cralley, T. E. Shea, and L. J. Cralley, *J. Ind. Hyg. Toxicol.*, *25*, 172 (1943).

[47c] H. H. Weber, *Chem.-Ztg.*, *57*, 836 (1933).

TABLE 26A

Color Reactions with Carbon Tetrachloride, Trichloroethylene, and Dichloromethane

Reagent	CCl_4	$ClCH:CCl_2$	CH_2Cl_2
I after boiling	Blue	Yellow-brown	Blue
I after addition of 85% H_2SO_4	Intense blue	Intense green-blue	Green-blue
I after addition of acetic acid	Red[a]	Yellowish	Yellow[a]
II after addition of acetic acid	Light brown	Green[a]	Yellowish
III after addition of acetic acid	Reddish yellow	Almost colorless	Colorless

[a] Especially characteristic reactions.

Place 30 ml. of glycol and some glass beads in a 250-ml. Erlenmeyer flask to serve as a bath. Place 2 drops of the chlorinated hydrocarbon in a large test tube, approximately 20 by 180 mm., add 2 ml. of a solution of 2 per cent phenolphthalein in cyclohexanol (III) and a pellet of sodium hydroxide. Place the test tube into the Erlenmeyer flask and equip the large test tube with a smaller one arranged to act as a condenser. Heat the bath and continue to heat for 5 minutes after the boiling begins, which is indicated by the sudden appearance of a violet color. Transfer the contents of the large test tube to an ordinary one, add 1 ml. of glacial acetic acid and some glass beads. Shake vigorously so that the crystals formed on cooling dissolve and compare with the colors noted in Table 26A.

5. *Ethyl Chloride*

Ethyl chloride, Kelene, C_2H_5Cl, is used industrially as a refrigerant, as an intermediate in the synthesis of other organic compounds, and fairly extensively in medicine as a local anesthetic. It is a gas at ordinary temperatures and pressures, having a boiling point of 12–13° C.; it has a specific gravity of 0.921 at 0° C.; and it is highly inflammable, having a lower inflammable limit of 4.0 and an upper limit of 14.8. It burns with a smoky green flame, with the production of toxic substances such as hydrochloric acid. It is slightly soluble in water and is miscible with alcohol and ether.

a. Physiological Response

The symptoms attending exposure of guinea pigs to ethyl chloride vapors are similar to those exhibited by exposure to methyl chloride.

except that the signs of lung irritation are not pronounced. Guinea pigs show greater signs of restlessness and excitement when exposed to ethyl chloride than when exposed to methyl chloride. Ethyl chloride gives some warning of its presence because it causes irritation, but a person might tolerate exposures to it in dangerous concentrations until helpless.

Guinea pigs died within a few minutes when exposed to concentrations of 15–30 per cent by volume. Exposure to concentrations of 6 to 10 per cent by volume for 30 to 60 minutes was dangerous to their life. The maximum concentration of ethyl chloride vapor tolerated for 60 minutes without serious disturbances was 4 per cent and the maximum concentration tolerated for several hours without or with but slight symptoms was 2 per cent by volume.[48]

Ethyl chloride is the least toxic of all the chlorinated hydrocarbons. The recommended maximum allowable concentration is 1,000 parts per million.

b. Determination

Ethyl chloride can be detected by the flame test and can be estimated by the general methods for the determination of solvent vapors in air. It can also be estimated by explosion methods, of which the following is a modification.[49]

If ethyl chloride is exploded with an excess of oxygen, the following reaction takes place:

$$C_2H_5Cl + 3O_2 \longrightarrow 2CO_2 + 2H_2O + HCl$$

Dilute the test sample in a gas-explosion pipette with a 1:1 oxygen-air mixture and then add electrolytic gas ($2H_2 + O_2$) to bring the mixture well within the flammable range. Explode the mixture. The combustion is generally complete and the reaction goes as indicated. After the explosion, note the contraction in volume. Absorb the carbon dioxide and the remaining hydrogen chloride, using caustic potash, and note the contraction again. Add the contraction resulting from the explosion and that attributable to absorption by the potash. This volume is used for determining the per cent of combustible material present in the mixture. The original paper should be consulted for the corrections to be applied.

Ethyl bromide, methyl chloride, methyl bromide, and ethylene dichloride may be estimated in a similar manner.

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[48] R. R. Sayers, W. P. Yant, B. G. H. Thomas, and L. B. Berger, *U. S. Pub. Health Service, Bull. 185* (1929).

[49] G. W. Jones, *Ind. Eng. Chem., 20,* 367 (1928).

6. 1,2-Dichloroethane (Ethylene Dichloride)

Ethylene dichloride is used principally as a solvent in the extraction of edible oils and fats, as a general solvent for rubber in the manufacture of dipped goods, and, in general, is finding increasing use as a substitute for other solvents because it is the most stable chlorinated hydrocarbon. It may be handled in the presence of water at boiling temperature in metal vessels without danger of corrosion.[50] It is used as a dewaxing agent because it is miscible in all proportions with mineral oil but is a poor solvent for the paraffin waxes. A mixture of 75 per cent ethylene dichloride and 25 per cent carbon tetrachloride, added to reduce the fire and explosion hazard, is used under certain conditions as a fumigant.[51] It has been used to kill moths in upholstered furniture, rolled rugs, sealed cartons, and similar places, and also for the fumigation of grain and flour to kill weevils. A mixture of the above proportions is marketed under the trade name "Chlorasol."

Ethylene dichloride (*sym*-dichloroethane, 1,2-dichloroethane, also known as Dutch Liquid, $ClCH_2CH_2Cl$) is a colorless liquid with a pleasant chloroform-like odor. It boils at 83–84°C.; has a specific gravity of 1.257 at 20/20° C.; a refractive index of 1.4443 at 20° C.; and a flash point of 15° C. It has a vapor pressure of 78 mm. of mercury at 20° C. and is, as the low flash point indicates, inflammable, with a lower limit of inflammability of 6.2 and an upper limit of 15.9. One volume is soluble in about 120 of water. It is miscible with alcohol, ether, and chloroform.

a. Physiological Response

Ethylene dichloride is an anesthetic, narcotic, and strong irritant. It has a hemolytic action about half as intense as that of chloroform. In a study of the physiological response of guinea pigs to inhalation of ethylene dichloride, the pigs exhibited the following symptoms:[52] eye and nose irritation, vertigo, static and motor ataxia, retching movements, semiconsciousness and unconsciousness accompanied by uncoordinated movements of the extremities, and death.

Exposure to 6 per cent caused all these symptoms, excepting death, to occur in less than 10 minutes, and death in about 30 minutes. Exposure to 1 per cent caused all the symptoms to appear in 25 minutes, with the possibilty of death occurring a

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[50] H. R. Fife and E. W. Reid, *Ind. Eng. Chem., 22,* 513 (1930).

[51] L. F. Hoyt, *Ind. Eng. Chem., 20,* 835 (1928).

[52] R. R. Sayers, W. P. Yant, C. P. Waite, and F. A. Patty, *U. S. Pub. Health Service, Reprint 1349* (1930).

> day or more following an exposure of about 15 to 20 minutes. Exposure to 0.12 per cent did not cause apparent symptoms or death following an exposure of 8 hours.
>
> A concentration of 10 to 20 per cent killed the pigs in a few minutes. Concentrations of 0.4 to 0.6 per cent were dangerous in 30 to 60 minutes. The maximum concentration tolerated by the pigs for 60 minutes without serious disturbances was 0.35 per cent and the maximum concentration producing but slight symptoms or no disturbance after several hours was 0.1 per cent.

In comparison with other harmful substances, ethylene dichloride appears to be of the same order of toxicity as benzene, carbon tetrachloride, and chloroform for periods of 1 hour or more of single exposures. For periods of less than 1 hour, this compound is less toxic than the others. It is one of the more toxic of the commonly used chlorinated hydrocarbons.[52a] The generally accepted maximum allowable concentration for an 8-hour daily exposure is 75 parts per million.

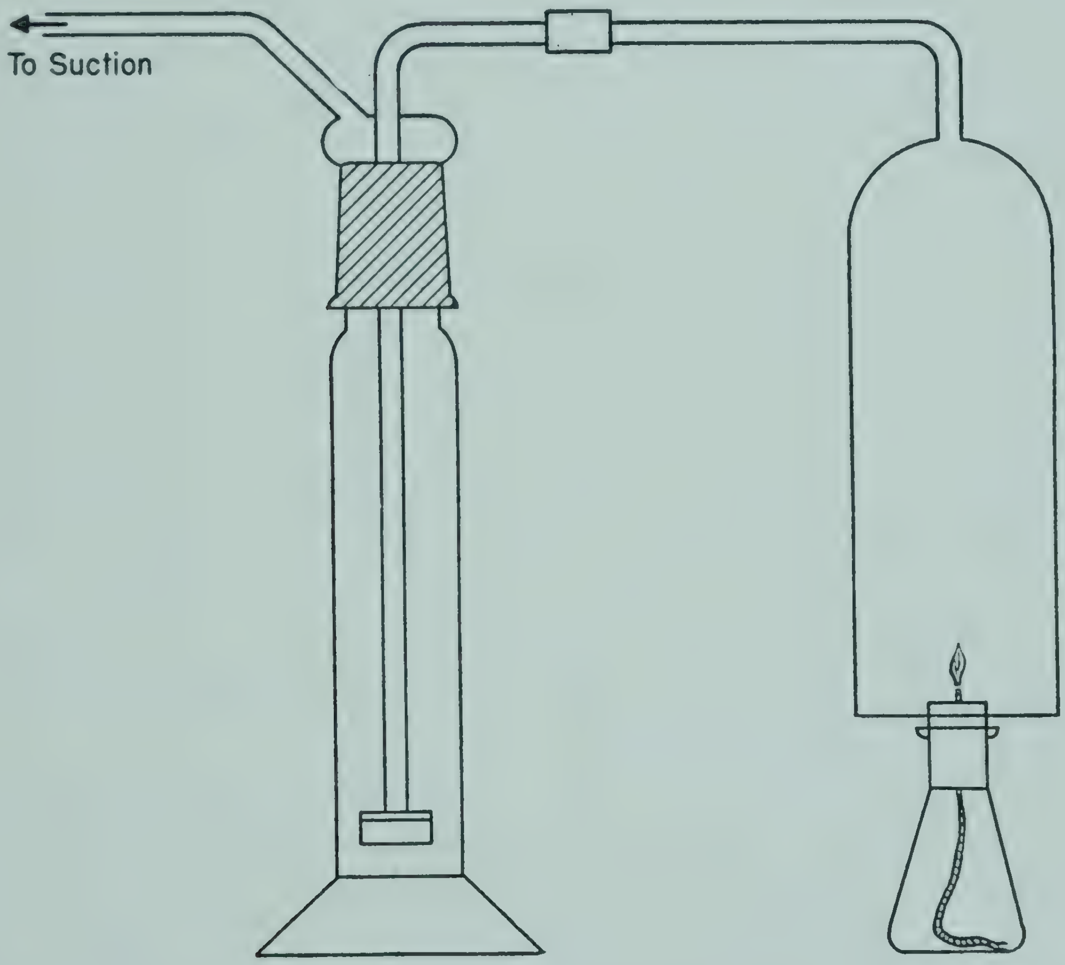

Fig. 116. Amyl acetate burner.

Ethylene dichloride has a distinct and noticeable odor and produces warning symptoms at relatively safe concentrations.

b. Detection and Determination

Ethylene dichloride can be detected by the flame test. Low concentrations of the vapor in air can be estimated by adsorption on air-equilibrated activated charcoal and silica gel and noting the gain in weight. High concentrations can be estimated by the use of an explosion pipette and electrolytic gas, and subsequent volumetric determination, as explained for ethyl chloride (page 579).

Goldman and Seegmiller[52b] modified the lamp method (page 588) for determining dichloroethane and found it to work well for concentrations of the order of 50 to 300 parts per million. Sampling was performed with two fritted-glass bubblers in series at a rate of 1 liter per minute at room temperature.

Make up the solvent to a fixed volume. Transfer a 10-ml. aliquot to a 25-ml. Erlenmeyer flask equipped with a cigarette-lighter wick, 3 mm. in diameter (Fig. 116). Ignite and allow to burn to completion, drawing air through the fritted-glass bubbler containing 125 ml. of 0.01 *N* sodium hydroxide solution at a rate of 2 liters per minute, which is adequate to keep the flame from being extinguished. The combustion requires about 2 hours.

7. 1,1-Dichloroethane

1,1-Dichloroethane, ethylidene chloride, CH_3CHCl_2 is a colorless liquid with an odor resembling chloroform. It boils at 57–59° C., has a specific gravity of 1.175 at 20° C., and has a refractive index of 1.4166. One part of ethylidene chloride is soluble in about 200 of water. It is miscible with alcohol.

The recommended maximum allowable concentration is 100 parts of 1,1-dichloroethane per million parts of air. It may be estimated by methods detailed in this chapter.

8. Tetrachloroethane

Tetrachloroethane, *sym*-tetrachloroethane, 1,1,2,2-tetrachloroethane. acetylene tetrachloride, $Cl_2CHCHCl_2$, is sold under many trade names. such as Cellon, Westron, Quittnerlack, Bonoform, Alanol, Novania, and others. It used to be called Tetraline but this name has been abandoned because of its similarity to Tetralin, or tetrahydronaphthalene. Among the uses to which this substance has been put may be mentioned its use as a solvent for fats, oils, cellulose acetate and nitrate, rubber, resins, tar

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[52a] L. A. Heppel, P. A. Neal, T. L. Perrin, K. M. Endicott, and V. T. Porterfield, *J. Ind. Hyg. Toxicol.*, *28*, 113 (1946); *J. Pharmacol. Exptl. Therap.*, *84*, 53 (1945).

[52b] F. H. Goldman and C. G. Seegmiller, *J. Ind. Hyg. Toxicol.*, *25*, 181 (1943).

pitch, waxes, and sulfur. It is used in the formulation of paint and varnish removers, in lacquers, floor waxes, rubber cements. It is employed in the artificial silk, artificial leather, artificial pearl, rubber, and safety-glass industries. It is also used as a dry-cleaning agent, as an insecticide, and as a fire extinguisher.

Tetrachloroethane is a colorless liquid with an odor resembling those of chloroform and carbon tetrachloride. The inhaled vapors have a sweetish taste. It boils at 146° C. and has a specific gravity of 1.60 and a refractive index of 1.4942 at 20° C. Its vapor pressure at 20° C. is 11 mm. of mercury. It is insoluble in water and is miscible with alcohol and ether. It is slowly hydrolyzed by water, with the formation of hydrochloric acid, and consequently is corrosive to metals.

a. Physiological Response

Tetrachloroethane is the most poisonous of the halogenated hydrocarbons.[53] It acts in two ways, attacking the nervous system and the gastrointestinal system. Among the symptoms exhibited by persons suffering from poisoning by this compound may be mentioned abnormal fatigue, profuse perspiration, nervousness, headache and vertigo, insomnia, gastrointestinal disorders including nausea and vomiting, blood disorders, abdominal pains, fatty changes in the viscera, especially the heart, yellow atrophy of the liver, and jaundice. In severe cases, death may ensue.[53] Its narcotic action is about four times as great as chloroform. The maximum allowable concentration is 5 parts per million parts of air.

b. Determination

The vapors of tetrachloroethane can be detected by use of the Beilstein flame test. It may be estimated by the general method for the determination of solvent vapors in air by adsorption on air-equilibrated activated charcoal or on silica gel. It can be estimated by the combustion method detailed for carbon tetrachloride on page 570. Concentrations ranging from 9 to 12,700 parts per million, equivalent to 0.062 to 87.3 mg. per liter, can be adequately determined by this method.[54] The sulfur-lamp combustion method of Elkins and his co-workers[55] (page 588) may also be used, as may the Fujiwara method modified by Barrett[56] (page 590).

[53] W. J. McConnell, *J. Am. Med. Assoc.*, *109*, 762 (1937).
[54] H. F. Smyth, *Ind. Eng. Chem.*, *Anal. Ed.*, *8*, 379 (1936).
[55] H. B. Elkins, A. K. Hobby, and J. E. Fuller, *J. Ind. Hyg. Toxicol.*, *19*, 474 (1937).
[56] H. M. Barrett, *J. Ind. Hyg. Toxicol.*, *18*, 341 (1936).

9. Pentachloroethane

Pentachloroethane, CCl_3CHCl_2, is used as a solvent in a manner analogous to tetrachloroethane. It is used as a solvent for cellulose acetate and as a dry-cleaning agent. It is known commercially as Pentalin. It is a colorless liquid with a chloroform-like odor. It boils at 161–162° C.; has a specific gravity of 1.6712 at 25/4° C.; and a refractive index of 1.5054 at 15° C.

It is a stronger narcotic than chloroform and almost as poisonous as tetrachloroethane, which it resembles as a metabolic poison. A concentration of 9,600 parts of pentachloroethane per million parts of air is lethal for most animals.[57] Lazarev[58] found that a concentration of 4,260 parts per million (35 mg. per liter) was the minimum lethal dose for mice.

Pentachloroethane may be detected and estimated by the methods described for its homologues. Since pentachloroethane has a trihalogenated carbon atom, it may be detected by the Fujiwara pyridine-sodium hydroxide reaction.[59] The details of this reaction are given for trichloroethylene (page 590).

10. 1,2-Dichloropropane (Propylene Dichloride)

Propylene dichloride, $CH_2ClCHClCH_3$, 1,2-dichloropropane, is a colorless liquid with an unpleasant odor in concentrated form. It has a specific gravity of 1.1583 at 20° C., boils at 96.8° C., and has a flash point, open cup, at 70° F. Its upper and lower limits of inflammability are 3.4 and 14.5 per cent, respectively. It is used as a component of cleansing and scouring mixtures, as a selective solvent, as an intermediate in the manufacture of organic chemicals, and in combination with dichloropropylene as a soil fumigant, particularly for killing nematodes on the roots of pineapple plants and for truck crops.

This material has caused cases of dermatitis in workers using it as a soil fumigant. The toxicology of propylene dichloride has been studied[59a] and it has been found that many deaths occurred among rats, guinea pigs, and rabbits receiving less than 8 exposures to concentrations of 2,000 parts per million. When a concentration of 1,500 parts per million was used, most of the animals were able to survive 35 exposures. At a concentration of 1,000 parts per million, deaths occurred among dogs after 24 exposures, among guinea pigs after 22 exposures, and among rats after as few as 7 exposures. Some of the animals survived 100 exposures. The recommended maximum allowable concentration is 75 parts per million.

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[57] K. B. Lehmann, *Arch. Hyg.*, *74*, 1 (1911).

[58] N. W. Lazarev, *Arch. exptl. Path. Pharmakol.*, *141*, 19 (1929).

[59] A. Brüning and M. Schnetka, *Arch. Gewerbepath. Gewerbehyg.*, *4*, 740 (1933).

[59a] L. A. Heppel, P. A. Neal, B. Highman, and V. T. Porterfield, *J. Ind. Hyg Toxicol.*, *28*, 1 (1946).

Its concentration in air may be determined by the methods detailed in this chapter.

11. Vinyl Chloride

Vinyl chloride, chloroethylene, $CH_2{:}CClH$ is used principally for the manufacture of organic synthetics like resins. It is a colorless gas at room temperatures with a pleasant ethereal odor. It boils at —14° C. It is inflammable, having a lower limit of inflammability of 4.0 and an upper limit of 21.7. It is slightly soluble in water and easily soluble in alcohol and other organic solvents.

Patty, Yant, and Waite[60] studied the physiological response of guinea pigs to vinyl chloride vapor. They found that the symptoms were principally those of narcosis. They ranged from unsteadiness and motor ataxia to incomplete and finally complete narcosis. The respirations of the pigs varied from a rapid jerky type accompanying the beginning of narcosis to a later slow, shallow type.

Exposure of the pigs to concentrations of vinyl chloride vapor of 20 to 40 per cent by volume was lethal in a very short time; 10 per cent was dangerous to the lives of guinea pigs after 30 to 60 minutes exposure. The maximum amount for an exposure of 1 hour without serious disturbances ranged from 1.0 to 1.5 per cent and the maximum concentration for several hours without acute disturbances of a serious nature was 0.5 per cent.

Vinyl chloride is less harmful than chloroform and carbon tetrachloride and is similar in toxicity to ethyl chloride. The recommended maximum allowable concentration is 500 parts per million. The danger from explosion exceeds the health hazard from exposure. Vinyl chloride does not possess adequate warning irritative properties but does produce dizziness which should warn except in very high concentrations, which cause almost immediate helplessness.

Determination

The concentration of the vapor of vinyl chloride in air can be determined with an explosion pipette by combustion with oxygen and electrolytic gas to energize the combustion. For mixtures containing insufficient oxygen for complete combustion of the vinyl chloride present, a known amount of additional air or pure oxygen must be mixed with the sample before adding the electrolytic gas. The concentration of vinyl chloride may also be obtained by the combustion methods detailed in this chapter.

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[60] F. A. Patty, W. P. Yant, and C. P. Waite, *U. S. Pub. Health Service, Reprint 1405* (1930).

12. Dichloroethylene

Dichloroethylene, acetylene dichloride, *sym*-dichloroethylene, ClHC:-CHCl, is used as an industrial solvent for fats, phenols, and camphor. It is also used as a dry-cleaning agent and as an insecticide and germicide. It is employed in the artificial-silk industry and in the perfume industry. It is sold under the commercial names of Dioform and Dielene.

It is a colorless liquid with an ethereal, slightly acrid odor. It boils at 55° C. and has a specific gravity of 1.28. The commercial product consists of a mixture of the *cis* and *trans* forms of dichloroethylene. It is insoluble in water but is soluble in alcohol, ether, and most other organic solvents. It is gradually decomposed by light, air, and moisture, with the formation of hydrochloric acid.

Dichloroethylene is a narcotic and anesthetic. It is considered less poisonous than carbon tetrachloride and more poisonous than chloroform by Lehmann,[61] but on the basis of recommended maximum allowable concentrations it is more toxic than chloroform; this value is 200 parts per million.

Dichloroethylene can be detected by the flame test and can be estimated by combustion methods. These methods are adequate in the range of 13–22,580 parts per million equivalent to concentrations of 0.051–89.5 mg. per liter.[62] The general methods for solvent vapors may also be used.

13. Trichloroethylene

Trichloroethylene, $ClCH:CCl_2$, is known commercially as Chlorylene, Tricline, Westrosol, Benzinol, Circosolv, Fleck-Flip, Blacosolv, Cecolene, Perm-A-Chor, Triclene, etc. It is used extensively for degreasing of metal parts and fat-free glue. It is used in many industries as a solvent and as a component of various products, among which may be mentioned the extraction of fats and oils, the extraction of resins, as a solvent for tar and pitch in the varnish and paint industry, the extraction of sulfur and phosphorus, and as a solvent for rubber in rubber cements. It is also used as an insecticide and as a dry cleaner.

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[61] K. B. Lehmann, *Arch. Hyg.*, *74*, 1 (1911).

[62] H. F. Smyth, *Ind. Eng. Chem., Anal. Ed.*, *8*, 379 (1936).

Trichloroethylene is a colorless liquid with a chloroform-like odor. It boils at 88–90° C.; has a specific gravity of 1.45 at 20/20° C.; and a refractive index of 1.4782 at 20° C. It is insoluble in water but is miscible with alcohol, ether, and oils. It is decomposed slowly by water or moisture, with the formation of hydrochloric acid and hence is often mixed with a stabilizing agent. It is noninflammable at ordinary temperatures but can be burned at elevated temperatures under proper conditions.

a. Physiological Response

Trichloroethylene is a narcotic and anesthetic. It is not only effective through inhalation but can also be absorbed[63] through the skin. McConnell[64] states that it is a nerve poison.

The symptoms produced by trichloroethylene poisoning in man are apparent drunkenness; stupor; dullness, dizziness, and confusion; nausea, vomiting, and gastrointestinal disturbances; irritation and nervous disorders; temporary unconsciousness, unconsciousness, and death.[65]

Lehmann[66] found the lethal dose for cats for exposures of 30 minutes to be 37,000 parts of trichloroethylene per million parts of air. Lazarev[67] found the lethal dose by inhalation to be 3,000–4,600 parts per million for mice after 2 hours, while Carrieu[68] obtained a value of 27,000 parts per million for the guinea pig.

Taylor[69] found that concentrations in air of 0.5–0.4 per cent of trichloroethylene vapor (5,000–4,000 parts per million) produced deep anesthesia in rats while 0.2 per cent (2,000 parts per million) gave slight narcosis. He found no liver or kidney injuries even after long exposure

According to Barrett and his co-workers,[70] carbon tetrachloride is considerably more toxic than trichloroethylene to guinea pigs and therefore the margin of safety is greater for this compound than for carbon tetrachloride. Seifter[70a] reported investigations with dogs. Morse and Goldberg[70b] noted the effects on human beings. The maximum allowable concentration recommended by government industrial hygienists for an 8-hour daily exposure is 150 parts of trichloroethylene per million parts of air.

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[63] C. P. McCord, *J. Am. Med. Assoc., 95,* 409 (1932).

[64] W. J. McConnell, *J. Am. Med. Assoc., 109,* 762 (1937).

[65] K. Stüber, *Arch. Gewerbepath. Gewerbehyg., 2,* 398 (1931).

[66] K. B. Lehmann, *Arch. Hyg., 74,* 1 (1911).

[67] N. W. Lazarev, *Arch. exptl. Path. Pharmakol., 141,* 19 (1929).

[68] M. F. Carrieu, *Rev. hyg. med. prevent., 49,* 348 (1927).

[69] H. Taylor, *J. Ind. Hyg. Toxicol., 18,* 175 (1936).

[70] H. M. Barrett, D. L. MacLean, and J. G. Cunningham, *J. Ind. Hyg. Toxicol., 20,* 360 (1938).

[70a] J. Seifter, *J. Ind. Hyg. Toxicol., 25,* 250 (1944).

[70b] K. M. Morse and L. Goldberg, *Ind. Med., Ind. Hyg. Supplement, 12,* 706 (1943).

b. Detection and Determination

Trichloroethylene gives the flame test and the Fujiwara pyridine-sodium-hydroxide reaction.[71] It can be detected by these tests. Trichloroethylene can also be estimated by combustion methods. Combustion methods were found to be applicable for concentrations ranging from 12–16,900 parts per million, equivalent to 0.066–90.7 mg. of trichloroethylene vapor per liter of air.[72] The method used for methyl chloride (page 562) is also applicable. A photometric method for the determination of trichloroethylene has been described in Chapter XII (page 489).

Rapid Combustion Method.[73] Trap the trichloroethylene vapors by passing the air to be tested through an efficient bubbler containing alcohol. Transfer an aliquot part by weight of the resulting alcoholic solution to an ordinary spirt lamp. Burn the alcoholic solution and trap the vapors which contain the decomposition products of trichloroethylene, namely hydrochloric acid, chlorine, and phosgene, in a standard solution of silver nitrate. Two scrubbers, each containing 25 ml. of 0.02 *N* silver nitrate solution, are generally sufficient for dilute concentrations, but for amounts exceeding 0.1 g. 0.1 *N* silver nitrate solution should be used. The products of the combustion are decomposed by water into hydrochloric acid and carbon dioxide. The excess standard silver nitrate solution is titrated in the usual way with standard 0.1 *N* or 0.02 *N* potassium thiocyanate solution. One ml. of 0.1 *N* silver nitrate solution is equivalent to 0.00438 g. of trichloroethylene.

Goldman and Seegmiller[73a] found that the spirit-lamp method was adequate for solvents like methyl and ethyl alcohol, which produce a hot flame, but that the lamp was inadequate for solvents like amyl acetate.

Sulfur-Lamp Method. The sulfur-lamp method for the determination of halogenated hydrocarbons depends upon the collection of the vapor in an organic solvent, its decomposition by burning the solvent, and the determination of the halide liberated.[74–76]

[71] A. Brüning and M. Schnetka, *Arch. Gewerbepath. Gewerbehyg.*, *4*, 740 (1933).
[72] H. F. Smyth, *Ind. Eng. Chem., Anal. Ed.*, *8*, 379 (1936).
[73] A. Dargie, *Analyst*, *62*, 730 (1937).
[73a] F. H. Goldman and C. G. Seegmiller, *J. Ind. Hyg. Toxicol.*, *25*, 181 (1943).
[74] W. M. Malisoff, *Ind. Eng. Chem., Anal. Ed.*, *7*, 428 (1935).
[75] C. Wirth, III, and M. J. Stross, *Ind. Eng. Chem., Anal. Ed.*, *5*, 85 (1933).
[76] H. B. Elkins, A. K. Hobby, and J. E. Fuller, *J. Ind. Hyg. Toxicol.*, *19*, 474 (1937).

Apparatus. The apparatus (Fig. 117) consists of an absorber of chemically resistant glass of about 150 ml. capacity containing glass beads or short pieces of rod in the suction side. It is connected to the source of suction through a Kjeldahl trap and to the lamp by a chimney of heat-resistant glass.

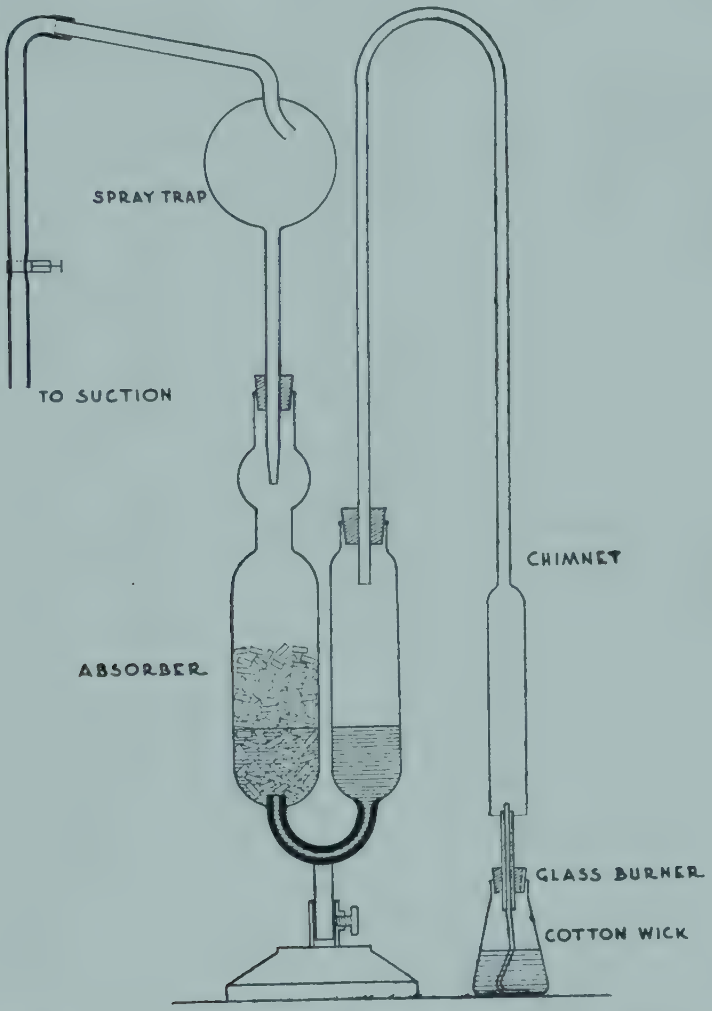

Fig. 117. Sulfur lamp for determination of chlorinated hydrocarbons.[76a]

The lamp burner consists of a 25-ml. Erlenmeyer flask equipped with a cork carrying a short section of glass tube about $^1/_8$ inch inside diameter which acts as the burner. The cork must be grooved along the sides so that air may enter the flask while the solvent is being consumed by the flame. A cotton wicking is inserted in the tube and rests in the solvent. A cigarette lighter wick is also suitable (see page 581).

[76a] After Am. Soc. Testing Materials, "Sulfur in Oils," *A. S. T. M. Tentative Standards* (1928).

Procedure. Pass 40 liters of air through 75 ml. of amyl acetate in a five-fold absorber (page 90) at a rate of flow of 1 liter per minute. Transfer the contents to another vessel. Rinse the absorber with amyl acetate and note the total weight of solvent solution. Burn a weighed aliquot of the amyl acetate for 2 hours in the sulfur-lamp apparatus and reweigh to obtain the weight of solvent consumed. At the same time burn a nearly equivalent amount of amyl acetate as a blank.

Transfer the contents of the sulfur-lamp absorber, which is charged with 25 ml. of 0.01 *N* sodium hydroxide solution, to a 200-ml. casserole. neutralize with 0.03 *N* nitric acid using methyl red as indicator, and then evaporate to 3–4 ml. Add a few drops of concentrated potassium dichromate solution, cool, and titrate with 0.01 *N* silver nitrate solution until a permanent red color is obtained. Perform the titration in yellow light, which improves the end point. One ml. of 0.01 *N* silver nitrate solution is equivalent to 0.000438 g. of trichloroethylene.

Colorimetric Method.[77–82] As in the case of chloroform and other compounds having three halogens attached to one carbon atom, trichloroethylene, though having the three halogens attached to two carbon atoms, also produces a color when heated with a mixture of pyridine and sodium hydroxide solution. The color produced with trichloroethylene is orange, in contradistinction to chloroform, which gives a red color. Furthermore, the color produced with trichloroethylene is fairly stable and will not be destroyed even upon heating in a water bath for 40 minutes, while that with chloroform is almost destroyed at the end of 5 minutes.

Sampling. Tubes of the type shown in Figure 118 may be used for absorbers. They should be filled with glass beads of 2–3 mm. diameter. Place the stopper in the tube and introduce 40 ml. of absolute alcohol through the top tube by means of a 10-ml. pipette. This fills the tube to a level just above the beads. The air to be analyzed is drawn through the absorber at a rate of from $^1/_3$ to 2 liters per minute. The volume of

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[77] H. M. Barrett, *J. Ind. Hyg. Toxicol., 18,* 341 (1936).

[78] K. Fujiwara, *Sitzber. Abhandl. naturforsch. Ges. Rostock, 6,* 1 (1914); *Chem. Abstracts, 11,* 3201 (1917).

[79] J. H. Ross, *J. Biol. Chem., 58,* 641 (1923–4).

[80] W. H. Cole, *J. Biol. Chem., 71,* 173 (1926).

[81] A. O. Gettler and H. Blume, *Arch. Path., 11,* 555 (1931).

[82] A. Brüning and M. Schnetka, *Arch. Gewerbepath. Gewerbehyg., 4,* 740 (1933).

gas aspirated is measured by collecting the water discharged from the aspirator in a 1-liter graduated cylinder. Satisfactory determinations may be obtained by the aspiration of as little as 1 liter of air when the concentration of the trichloroethylene vapor is high. With lower concentration it is necessary to utilize larger air samples. All of the trichloroethylene is trapped by a single tube when the concentration in the sample is not over 1,500 parts per million and the rate of aspiration is not greater than 2 liters per minute. Otherwise a train of traps must be used.

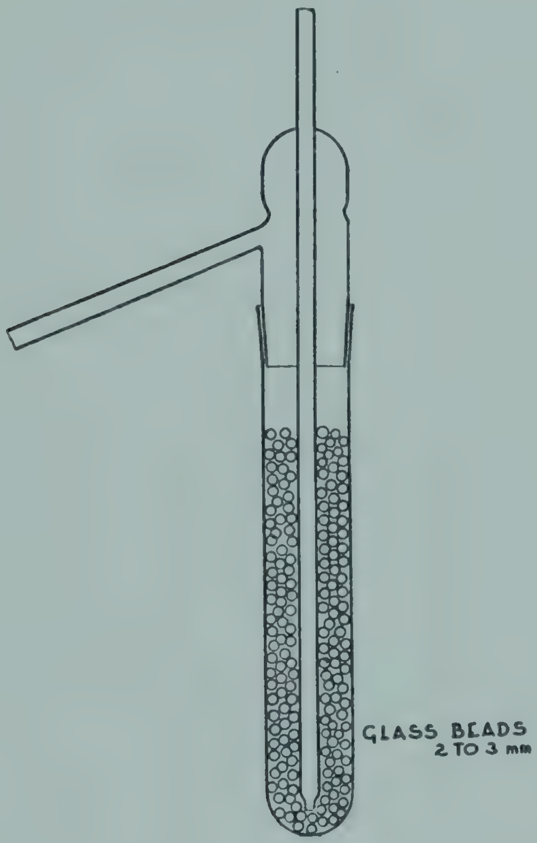

Fig. 118. Absorption tube.

Fujiwara[78] and Cole[80] point out that the test is more sensitive in aqueous solution, but the insolubility of trichloroethylene in water makes it necessary to use alcohol as an absorbing medium. By diluting the alcohol to a concentration of 20 per cent by volume, the accuracy of the test is enhanced, for both the sensitivity and the ease with which the colors may be matched are increased.

Preparation of Standards. Stock Solution A.—Pipette 1 ml. of commercial trichloroethylene into a 100-ml. volumetric flask and fill to the mark with absolute alcohol.

Stock Solution B.—Dilute 2 ml. of solution A to 200 ml. with 20 per cent alcohol solution. Place 5, 10, 20, 30, and 40 ml. of solution B in 50-ml. volumetric flasks and dilute to the mark with 20 per cent alcohol solution. This gives a set of standards containing 10, 20, 40, 60, and 80 parts trichloroethylene per million. These standards should be kept tightly stoppered and must be prepared fresh each day that the test is to be carried out.

Procedure. Disconnect the absorber from the aspirator and shake thoroughly. Transfer 10 ml. of the alcohol containing the absorbed trichloroethylene to a 50-ml. volumetric flask and dilute to the mark with water. Stopper the flask tightly and shake.

Pipette 5 ml. of each of the standards into 8- by 1-inch Pyrex test tubes. Add 2 ml. of colorless pyridine and 3 ml. of 50 per cent sodium hydroxide solution to each tube by means of burettes. Treat 5 ml. of the diluted sample solution in the same way. Stopper the tubes with cotton wool and shake thoroughly, being careful not to wet the cotton wool. Place the tubes in a metal rack and suspend the rack in a boiling-water bath for 5 minutes. After removal from the bath, cool the tubes in running water for 3 to 5 minutes and compare the color of the supernatant layer of the test solution with the standards. Calculate the concentration of the trichloroethylene in the air sampled from the concentration of the nearest standard. Multiply the result by a correction factor 0.68.

For example, if in a given test, the 50 parts per million by volume standard (5×10^{-5}) yields the same intensity of color as the unknown prepared from the absorber tube, through which 3 liters of air had been aspirated, then

$$\text{trichloroethylene content per liter of air} = \frac{200 \times 5 \times 10^{-5} \times 1.46}{3}$$
$$= 4.9 \text{ mg. per liter}$$

The density of trichloroethylene is 1.46.

Solutions and standards should be kept stoppered with cotton wool as much of the time as possible to minimize loss of trichloroethylene by evaporation. Pipetting and addition of reagents should be done as quickly as possible for the same reason. It is very important to have simultaneous heating of the unknown and standards, for the shade of color varies with the time of heating. The method is correct to about ±20 per cent of the concentration of vapor in the air but this accuracy is sufficiently great for field work. Because of the comparatively large error of the method there is no advantage in using a colorimeter instead of visual comparison. The method will detect concentrations as low as 20 parts per million.

14. Tetrachloroethylene

Tetrachloroethylene, carbon dichloride, perchloroethylene, $Cl_2C:CCl_2$, is used commercially as a solvent, degreaser, and dry cleaner. It is a colorless liquid with an ethereal odor. It boils at 121° C. and has a specific gravity of 1.60–1.61 at 25/25° C. and a refractive index of 1.5018 at 20° C. One part of perchloroethylene is soluble in about 10,000 parts of water. It is miscible with alcohol, ether, chloroform, and benzene. It is a nonflammable substance at ordinary temperatures but can be decomposed and burned at higher temperatures.

Perchloroethylene is similar in its physiological action to chloroform and carbon tetrachloride.[83] The recommended maximum allowable concentration is 100 parts per million.

The concentration of perchloroethylene vapor in air can be estimated by the general methods for solvent vapors given in Chapter XII and by the combustion methods described in this chapter. Smyth[84] found combustion methods to be adequate in the range of concentrations from 11–12,700 parts of perchloroethylene vapor in one million parts of air. This is equivalent to a range of 0.073–86.2 mg. per liter.

The R & H Tri-Per Analyzer is an instrument especially designed to estimate photoelectrically the concentration of perchloroethylene in air. It is briefly described in Chapter XII (page 489).

15. Allyl Chloride

Allyl chloride, 3-chloropropene, $CH_2:CHCH_2Cl$, is used as a chemical intermediate and in the manufacture of synthetic perfumes. It is a colorless liquid with an unpleasant odor. It boils in the range 44.8–45.3° C.; has a specific gravity of 0.9374 at 20/4° C.; and a refractive index of 1.4155 at 20° C. It is slightly soluble in water, miscible with alcohol, chloroform, ether, and petroleum ether.

Allyl chloride appears to be among the most toxic of the halogenated aliphatic hydrocarbons having a strong irritating action.[85] Rats and guinea pigs exposed to 100, 50, 20, and 10 mg. per liter showed irritation of the mucous membranes within a few minutes. The narcotic action was weak. It produced lesions of the lungs and kidneys and slight changes in the liver. Some deaths occurred even with concentrations of 1 mg. per liter for exposure of 4 hours. A maximum allowable concentration of 50 parts per million has been suggested in California.

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[83] F. Flury and F. Zernik, *Schaedliche Gase*, Springer, Berlin, 1931.

[84] H. F. Smyth, *Ind. Eng. Chem., Anal. Ed., 8,* 379 (1936).

[85] E. M. Adams, H. C. Spencer, and D. D. Irish, *J. Ind. Hyg. Toxicol., 22,* 79 (1940).

The concentration of this vapor in air can be determined by the general methods of adsorption detailed in Chapter XII and by combustion methods.

16. Chloroprene

Chloroprene, 2-chloro-1,2-butadiene ($CH_2:CHCCl:CH_2$), 2-chlorobutadiene, is used in ever-increasing amounts in industry, for it is a starting material for the manufacture of synthetic rubber, for instance, Duprene.

It is a colorless liquid which boils at 59.4° C. and has a specific gravity of 0.9583 20/20° C. and a refractive index of 1.4583 at 20° C. It is very slightly soluble in water but is miscible with alcohol and ether and is soluble in most organic solvents.

Experiments indicate that chloroprene is a toxic material.[86] Contamination of the skin and hair should be avoided and the inhalation of vapor concentrations as low as 0.3 mg. of chloroprene per liter of air, equivalent to 83 parts of chloroprene per million parts of air, may cause toxic symptoms. The recommended maximum allowable concentration is 25 parts per million. Early detection of incipient poisoning is possible because of alteration of the icteric index, the presence of albumin, reducing substances and bile pigment in the urine and a lowering of the blood pressure. Other indicative symptoms are loss of appetite, indigestion, and catarrhal condition of the respiratory tract.

The concentration of the vapor of chloroprene in air can be estimated by methods previously described in this chapter, by the adsorption methods and the photoelectric methods described in Chapter XII.

17. Chlorobenzene

Chlorobenzene, monochlorobenzene, is used industrially as a solvent for cellulose acetate, artificial resins, oils and fats, etc. During World War I it was used as a solvent for dichloroethylsulfide (mustard gas), which melts at 14° C., in order to lower the melting point of this chemical-warfare agent. It is also used as a component of lacquers, a component of fast-drying inks, and as a dry-cleaning compound.

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[86] W. F. von Oettingen, W. C. Hueper, W. Deichmann-Gruebler, and F. H. Wiley, *J. Ind. Hyg. Toxicol.*, *18*, 240 (1936).

It is a colorless liquid with a faint odor. It boils at 131–132° C. and has a specific gravity of 1.107 at 20/4° C. and a flash point of 28° C. It is insoluble in water but is freely soluble in alcohol, benzene, chloroform, and ether.

a. Physiological Response

Chlorobenzene is about as toxic as benzene. Flury and Zernik[87] rate it as more toxic, whereas Hamilton[88] rates it as less toxic than benzene. Goetzmann[89] found the lethal dose for cats to be 3,700 parts of chlorobenzene per million of air, that is, 17 mg. per liter, for exposures of 7 hours. The maximum tolerated for 1 hour was 220–660 parts per million; severe symptoms were caused by exposure to 8,000 parts per million, with exposure for 30 minutes followed by death within 2 hours after removal. The recommended maximum allowable concentration is 75 parts per million.

b. Detection and Determination

Chlorobenzene gives the Beilstein flame reaction. It also can be detected by the butanone method described for toluene (page 540). It may be estimated by the general methods for solvent vapors described in Chapter XII and by combustion methods detailed in this chapter. Smyth[90] states that combustion methods are adequate in the concentration range from 12–18,500 parts of chlorobenzene in one million parts of air. This is equivalent to concentrations of 0.054–85.0 mg. per liter.

18. Dichlorobenzene

o-Dichlorobenzene. This is a liquid at ordinary temperatures, for it has a melting point of —17.5° C. It is used principally as a fumigant and a dyestuff intermediate. It is also used in metal degreasing, for removing sulfur from illuminating gas and as a component of lacquers and varnishes. The commercial compound contains considerable amounts of chlorobenzene, *p*-dichlorobenzene, trichlorobenzene, and other chlorinated compounds.

It boils at 180–183° C.; has a specific gravity of 1.307 at 20/20° C.;

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[87] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

[88] A. Hamilton, *Industrial Toxicology*, Harper, New York, 1934.

[89] E. Goetzmann, quoted by K. B. Lehmann and F. Flury, *Toxikologie und Hygiene der technischen Lösungsmittel,* Springer, Berlin, 1938.

[90] H. F. Smyth, *Ind. Eng. Chem., Anal. Ed., 8,* 379 (1936).

a refractive index of 1.5518 at 22° C.; and a flash point of 27° C. It is insoluble in water and is miscible with alcohol, ether and benzene.

o-Dichlorobenzene is similar in toxicity to monochlorobenzene. The lethal concentration in air is about 2.5 times that of carbon tetrachloride. It is less toxic than tetrachloroethane.[91] The recommended maximum allowable concentration is 50 parts of *o*-dichlorobenzene per million parts of air.

The concentration of *o*-dichlorobenzene can be determined by the methods previously detailed in this chapter and in Chapter XII.

***p*-Dichlorobenzene.** *p*-Dichlorobenzene is being used increasingly as an insecticide and vapor fumigant. It is a colorless or white crystalline solid which melts at 53° C.; boils at 174° C.; has a specific gravity of 1.458 at 20/4° C.; a refractive index of 1.5266 at 70° C.; and a flash point of 67° C. It is practically insoluble in water but is freely soluble in alcohol, ether, chloroform, and carbon disulfide.

Its physiological response is similar to that of monochlorobenzene and *o*-dichlorobenzene.[92]

Determination

The concentration of *p*-dichlorobenzene can be estimated by the following modification of the general method for solvent vapors in air, in which the vapor is frozen out in a tared trap and then weighed.[93]

Pass the sample of air through a long tube, 20–24 in., containing flake sodium hydroxide to remove moisture, at a rate of 18 liters per hour, and then through a tared condensing device immersed in a solid carbon dioxide-alcohol freezing bath. Disconnect the condensing device, turn the stopcock or other closing equipment, allow to come to temperature, and weigh. The gain in weight less a blank run on air containing no *p*-dichlorobenzene is equivalent to the weight of *p*-dichlorobenzene in the sampled air.

The concentration of *p*-dichlorobenzene can also be obtained by combustion methods such as heating in a quartz tube at 1000° C., absorbing the chlorides in alkaline sulfite solution, and estimating the chlorides by the Volhard method.[94]

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[91] E. Browning, *Toxicity of Industrial Organic Solvents,* Chemical Publishing, New York, 1938.

[92] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931

[93] F. R. Darkis, H. E. Vermillion, and P. M. Gross, *Ind. Eng. Chem.*, *32*, 946 (1940).

[94] W. A. Van Winkle and G. McT. Smith, *J. Am. Chem. Soc.*, *42*, 333 (1920)

19. Chlorinated Naphthalenes and Diphenyls[95,96]

Chlorinated naphthalenes and diphenyls, because of their electrical-, heat-, and moisture-resisting properties, and because they are noninflammable, are used extensively for insulating wire and in the manufacture of electrical condensers. The chlorinated naphthalenes are compounds in which one or more of the hydrogen atoms of naphthalene have been replaced by chlorine, forming a series from monochloronaphthalene to octochloronaphthalene. The chlorinated naphthalenes as used commercially are mixtures of chloronaphthalenes. Thus commercial trichloronaphthalene is a mixture of the tri and tetra derivatives containing approximately 50 per cent chlorine. A mixture consisting of tetra-, penta-, and hexachloronaphthalene in combination with chlorinated diphenyls is also commonly used.

In the manufacture of the chlorinated diphenyls, benzene is converted into diphenyl by passing it through molten lead. Chlorine is then bubbled through, displacing one or more of the hydrogen atoms, forming derivatives ranging from monochlorodiphenyl to decachlorodiphenyl, in which all of the hydrogen atoms have been displaced.

The higher the chlorination, the higher the melting point of the artificial wax and the more waterproof it becomes. Since resistance to heat and moisture are the most desirable characteristics of these products, the higher chlorinations are those most in demand commercially.

The chlorinated naphthalenes are commonly referred to as "Halowax." This term is a trade name of the Halowax Corporation and should not be used to designate the chlorinated naphthalenes as a class.

a. Physiological Response

One of the marked effects of exposure to the chlorinated naphthalenes and diphenyls is a characteristic dermatitis.[97] During World War I, when perchloronaphthalene (Perna) was used as a rubber substitute in Germany, it was noted that workers contracted this type of acneform skin eruption.[97]

The serious internal injurious effects of these chlorinated compounds are manifested in the liver, with the production of yellow atrophy of

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[95] L. Greenburg, M. R. Mayers, and A. R. Smith, *N. Y. State Ind. Bull., 18,* 343 (1939).

[96] M. R. Mayers and Silverberg, *N. Y. State Ind. Bull., 17,* 358 (1938).

[97] L. Schwartz, *U. S. Pub. Health Service, Bull. 229* (1936).

the liver.[98] The toxicity of these compounds increases with increasing degree of chlorination. The chlorinated diphenyls are most injurious.

The accepted safe maximum permissible working concentration as shown in Table 6, Appendix, is 1.0 mg. per cubic meter for chlorodiphenyls, 0.5 mg. per cubic meter for chlorinated naphthalenes calculated as pentachloronaphthalene, and 5.0 mg. per cubic meter for chlorinated naphthalenes calculated as trichloronaphthalene. Drinker[98a] has suggested maximum allowable concentrations for these substances.

b. Determination

Since the chlorinated naphthalenes and diphenyls are mixtures, analytical methods can be used only to obtain the percentage chlorine. In the method of Millhiser and Hemperly[98] the air is passed over heated platinum in an electrically heated quartz tube and the effluent gas is scrubbed in a column of glass beads (Fig. 119) moistened with sodium carbonate containing a trace of sodium sulfite. The beads are washed down and the chlorine is determined nephelometrically.

Lamp Combustion Method. The following method is the variation of the lamp combustion method used by the Connecticut State Department of Health, Bureau of Industrial Hygiene.[98c] Decomposition of chlorinated naphthalenes and diphenyls by this method is not complete, for samples containing 50 to 60 per cent chlorine yield only 40 to 50 per cent.

Sampling. Draw the air sample through a sintered glass plate absorber containing 75 ml. of amyl acetate at a rate of about 10 liters per minute. A 30-minute sample is generally adequate but, as usual, low concentrations require a longer sampling period.

Procedure. Concentrate the sample by distillation in a 50-ml. distillation flask. Fill the flask half full with the sample and distill until the residual volume is not less than 4 ml. Allow to cool, half fill again, and repeat until the entire sample is concentrated to about 4 ml. Transfer the residue to a tared lamp burner, rinse the flask with about 4 ml. of the distillate, adding the rinse to the lamp, and weigh again.

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[98] G. A. Bennett, C. K. Drinker, and M. F. Warren, *J. Ind. Hyg. Toxicol.*, *20*, 97 (1938).

[98a] C. K. Drinker, *J. Ind. Hyg. Toxicol.*, *21*, 155 (1939).

[98b] After C. K. Drinker, M. F. Warren, and G. A. Bennett, *J. Ind. Hyg. Toxicol.*, *19*, 283 (1937).

[98c] A. S. Gray, J. Bernsohn, O. W. Boies, A. L. Coleman, R. M. Elrick, E. Glanz, A. E. Goss, L. Press, R. A. Schaefer, and G. H. Vance, *Methods for Determining Toxic Substances in Industrial Atmospheres and Materials.* Conn. State Dept. Health, Hartford, 1947.

Concentrate a blank of the same stock amyl acetate in the same manner, using a volume equal to that of the sample.

Burn the sample and the blank to dryness in the sulfur lamp apparatus described in the section on trichloroethylene in this chapter, charging the absorber with 25 ml. of 0.05 *N* sodium hydroxide solution making certain that an excess of sodium hydroxide is present at all times. Disconnect the absorption apparatus and rinse with several washings into a porcelain casserole. If the titration is to be performed potentiometrically, make the sample definitely acid to indicator paper, bringing the pH to below pH 4 with 0.25 *N* nitric acid. If a Mohr titration is to be made, carefully neutralize the sample to methyl red indicator and evaporate to about 2 ml. Cool and titrate with 0.01 *N* silver nitrate solution.

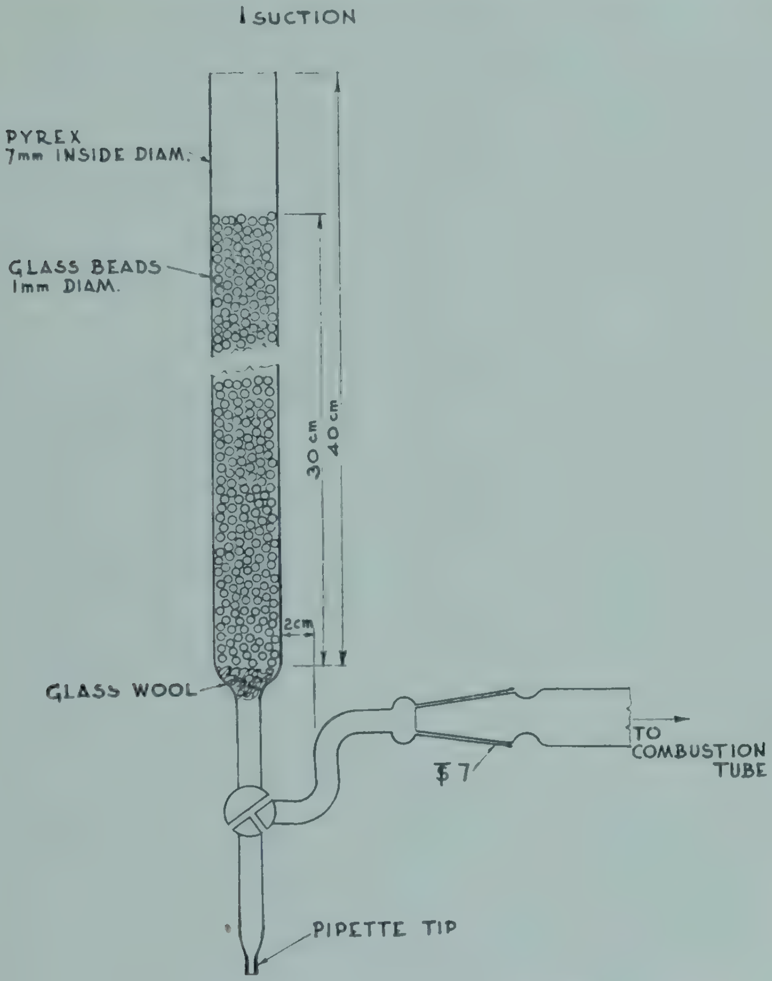
SUCTION
PYREX
7mm INSIDE DIAM.
GLASS BEADS
1mm DIAM.
30 cm
40 cm
2cm
GLASS WOOL
$ 7
TO
COMBUSTION
TUBE
PIPETTE TIP

Fig. 119. Absorption apparatus.[98b]

Calculation.

$$\text{Ml. } AgNO_3 \text{ equivalent to chlorides present in air} = A - (B \times C)$$

$$\frac{\text{Mg. chlorinated naphthalenes}}{\text{or diphenyls per cu. m. air}} = \frac{\text{ml. } AgNO_3 \times N\ AgNO_3 \times 35.5 \times 103}{\text{liters air sampled} \times F}$$

where:

A = ml. $AgNO_3$ required in titration of sample
B = ml. $AgNO_3$ per gram of blank burned
C = total weight of sample
F = fraction chloride contained in the compound

The concentrations of these substances can also be determined by the combustion method of Tebbens (page 570) and analogous combustion methods.

B. BROMINATED HYDROCARBONS

1. Methyl Bromide

Methyl bromide is used as a refrigerant and fumigant. Methyl bromide, bromomethane, CH_3Br, is a colorless gas at ordinary temperatures and when liquefied is a colorless liquid. It boils at 4.5° C. It is slightly soluble in water and freely soluble in alcohol, chloroform, ether, and carbon disulfide. Methyl bromide is ordinarily considered noninflammable and in fact was used in fire extinguishers[99] such as "Poleo" and "Ardex" as a component and as the sole agent in "Custos." However, Jones[100] shows that it has a very limited explosive range with a lower limit of 13.5 and an upper limit of 14.5. Flame and hot surfaces decompose it to hydrobromic acid, bromine, and other irritant gases.

a. Physiological Response

The toxicity and potential dangers of methyl bromide with reference to its use in chemical industries, as a fumigant, and in fire extinguishers have been reviewed by von Oettingen.[101] It is a highly toxic material of insidious action. The odor of methyl bromide is not distinctly unpleasant and therefore it cannot give definite warning of its presence in dangerous concentrations. Methyl bromide causes narcotic effects and more or less permanent damage to the nervous system. There is a definitely delayed toxic action following exposure to its vapors.[102,103] The recommended maximum allowable concentration is 20 parts per million.

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[99] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.
[100] G. W. Jones, *Ind. Eng. Chem., 20,* 367 (1928).
[101] W. F. von Oettingen, *U. S. Pub. Health Service, Nat. Inst. Health Bull. 185* (1946).
[102] A. Hamilton, *Industrial Poisons in the United States,* Macmillan, New York, 1925
[103] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

b. Detection

Flame Test. A simple procedure capable of indicating quickly the presence of dangerous concentrations of halide vapors in air is the Beilstein flame test.[104] All that is necessary is a flame impinging on a copper strip. In the presence of an atmosphere containing methyl bromide or other halide vapor, the flame becomes green or blue. However, it has been shown that under ideal lighting conditions and in the absence of air currents, such lamps can detect about 50 parts per million of methyl bromide. Concentrations below 35 parts per million give unreliable tests.[105] Jones and Kennedy[105a] describe a halide lamp in which adsorbent charcoal is used to adsorb halide gases in an atmosphere. The charcoal is then heated in a flame in contact with a copper screen. As little as 1 part per million can be detected. Timmis[105b] devised a blow lamp shielded from strong daylight for the detection of halide gases.

A commercial torch[106] with a self-generating burner equipped with a sampling tube and a copper reaction plate, designed for the detection of halide refrigerant leaks, may be used. Such torches should not be used for the detection of leaks of combustible gases like ethyl and methyl chloride.

The sensitivity varies with different rates of combustion, maximum sensitivity being obtained with a low flame. The valve of the burner should be adjusted so that with pure air the inner flame just disappears within the copper cone. Under these conditions the outer flame exhibits colors tabulated in Table 27 when air containing methyl bromide enters the sampling tube.

Solutions of monobromobenzene in clear heavy paraffin oil may be used as comparison standards for indicating the appearance of the flame color at various concentrations. Add the volumes of bromobenzene listed in Table 27 to 100-ml. portions of the oil. Keep the mixtures in 500-ml. containers and shake well before the comparisons are made. The vapor pressure of bromobenzene above each solution at the given temperature is such that when the sampling tube is inserted, the flame assumes the characteristic color shown by the corresponding methyl bromide-air mixture.

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[104] V. A. Stenger, S. A. Shrader, and A. W. Beshgetoor, *Ind. Eng. Chem., Anal. Ed., 11*, 121 (1939); *14*, 1 (1942).

[105] H. C. Dudley, J. W. Miller, P. A. Neal, and R. R. Sayers, *U. S. Pub. Health Repts., 55*, 2251 (1940).

[105a] G. W. Jones and R. E. Kennedy, *U. S. Bur. Mines, Rept. Invest. 3697* (1943).

[105b] L. B. Timmis, *J. Soc. Chem. Ind., 64*, 32 (1945).

[106] This torch, known as the Prest-O-Lite Halide Leak Detector, is available from the Linde Air Products Co., New York, N. Y.

Contamination of the sampling tube of the detector torch must be avoided, and any copper bromide present must be allowed to burn out of the torch between analyses. The air drawn through the standards must be free from methyl bromide. Light conditions under which samples and standards are observed should be as nearly identical as possible.

TABLE 27

Detection of Methyl Bromide with Lamp[104]

Methyl bromide concn.[a] ppm.	Flame color	Monobromobenzene, ml./100 ml. mineral oil	
		20° C.	30° C.
0	Almost invisible	0	0
50	Faint green	0.9	0.5
100	Moderate green	1.8	0.9
200	Strong green with trace of blue	3.5	1.8
500	Blue-green	8.5	4.3
1,000	Strong blue	17.0	8.5

[a] Concentrations expressed in parts per million by volume have been calculated for 760 mm. of mercury and 25° C., assuming the ideal gas law to be valid.

A green flame indicates a concentration above the maximum allowable concentration.

c. Determination

Ethanolamine Method.[104] Methyl bromide is hydrolyzed at room temperature by ethanolamine, $NH_2CH_2CH_2OH$. The bromide ion formed can then be estimated by the Volhard method or by the Kolthoff and Yutzy[107] modification of the van der Meulen method.[107a]

In the Volhard procedure, after hydrolysis with ethanolamine the bromide is estimated by precipitation with excess standard silver nitrate solution and subsequent titration of the excess silver solution by means of standard potassium thiocyanate solution.

In the Kolthoff-Yutzy procedure, the ethanolamine is eliminated by evaporation, then the dry material is dissolved in water, the bromide present is oxidized to bromate with sodium hypochlorite solution in slightly acid solution, and then the excess hypochlorite is destroyed by the use of sodium formate solution.[108] Iodide is added and the liberated iodine is estimated by titration with standard sodium thiosulfate solution.

[107] I. M. Kolthoff and C. H. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, *9*, 75 (1937).

[107a] J. H. van der Meulen, *Chem. Weekblad*, *28*, 82 (1931).

[108] R. L. Busbey and N. L. Drake, *Ind. Eng. Chem., Anal. Ed.*, *10*, 390 (1938).

Sampling. For sampling use 2-liter evacuated bottles equipped with stopcocks through which 2 ml. of ethanolamine may be introduced after sampling. Other bottles or separatory funnels may be used but these must be well flushed with the atmosphere to be tested. The reagent ethanolamine is added to these containers by means of a small soft-glass bulb containing 2 ml. of the compound. Close the stoppers and stopcocks and shake sufficiently hard to break the glass bulb.

After an interval of 15 minutes or longer the reaction between the ethanolamine and the methyl bromide may be considered complete and the bromide ion may be estimated.

Volhard Procedure. Wash down the stopper and sides of the flask or bottle and add a measured volume of standard 0.02 or 0.1 *N* silver nitrate solution depending upon the amount of bromide present. Add sufficient 6 *N* nitric acid to provide 1–3 ml. in excess. At this point silver bromide precipitates if methyl bromide was present in the sample. Titrate the excess silver nitrate solution with standard 0.02 or 0.1 *N* potassium thiocyanate solution, using 5 ml. of saturated ferric ammonium sulfate solution as indicator.

Run a blank on the same volume of ethanolamine, subjecting it to the same procedure and reagents as above, and adjust the calculation to account for any blank result, because ethanolamine slightly retards the end point. Ethanolamine also sensitizes silver bromide to the action of light, which should therefore be avoided as much as possible. Dark precipitates may be filtered off before titration of the excess silver nitrate solution. One ml. of 0.10 *N* silver nitrate is equivalent to 9.50 mg. of methyl bromide, and mg. of methyl bromide multiplied by 258 is equivalent to parts per million calculated for 760 mm. of mercury and 25° C.

Kolthoff-Yutzy Procedure. Wash the hydrolyzed sample into a 250-ml. flask and add 0.5 ml. of saturated sodium chloride solution and approximately 0.5 g. of sodium bicarbonate. Evaporate over a flame or on a hot plate in a well-ventilated hood to remove the dense fumes of ethanolamine. Reduce the volume to not less than 10 ml., then continue the evaporation to dryness while blowing steam through the flask. The steam displaces the air and sweeps out the vapors. Swirl the flask constantly to prevent bumping and drive off all the ethanolamine on the sides of the flask. Allow the flask to cool with the steam off, and then pass steam in again to dissolve the salts without the aid of external heat. Rinse the steam tube with water and bring the volume of the solution to 50 ml.

Add to the solution 2.5 ml. more of saturated sodium chloride solution, about 1 g. of sodium acid phosphate ($NaH_2PO_4.H_2O$ crystals), and 2 ml. of 1 *N* sodium hypochlorite solution in 0.1 *N* sodium hydroxide solution. Heat the mixture to boiling. After a minute or so, add 2 ml. of sodium formate solution, 50 g. of sodium formate, HCOONa, dissolved in water and diluted to 100 ml., and continue boiling for 2 minutes more. Cool the solution, dilute to 75 ml., and add 1 drop of sodium molybdate solution, 1 g. of sodium molybdate, Na_2MoO_4, dissolved in water and diluted to 100 ml. Add 0.5 g. of potassium iodide and 10 ml. of 6 *N* sulfuric acid and titrate immediately with standard 0.01 *N* sodium thiosulfate solution, adding 1 per cent starch solution just before the end point. A blank on an equivalent amount of ethanolamine with all other reagents should be carried through the entire procedure and subtracted from the test result. One ml. of 0.010 *N* thiosulfate solution is equivalent to 0.1583 mg. of methyl bromide.

Combustion Modification. To avoid the use of monoethanolamine, Williams[108a] used a combustion furnace to decompose the methyl bromide. This furnace was made by winding resistance wire around a 20-cm. length of 2.5-cm. quartz tubing and insulating with Alundum cement and magnesia pipe lagging. The voltage to the furnace was controlled by means of a Variac, type 200-CM. The temperature was measured by means of a chromel-alumel thermocouple and a milliammeter. The combustion tube was a 50-cm. length of 4-mm. inside diameter quartz tubing bent at a 90-degree angle 2.5 cm. from the exit end. The tube should extend at least 6 inches beyond the furnace on the exit side to permit dissipation of the heat of the gases. Williams used a diffuser prepared from a 6- by 37-mm. Alundum extraction thimble No. RA98 sealed to the end of a 32-mm. length of 7-mm. glass tubing and an absorber made from a 14-cm. length of 14-mm. glass tubing.

Procedure. Set up the combustion furnace, absorber, flowmeter, and a Hoke straight needle valve, 0.3 cm., V-point, No. 341, in the order given. Charge the absorber with 10 ml. of 0.1 *N* sodium hydroxide solution and connect the inlet side of the furnace to the position to be tested by means of Saran tubing. Heat the furnace, turn on the needle valve, adjust the airflow to 500 ml. per minute, and start a stop watch simultaneously. Continue sampling for 4 minutes or longer, depending on the expected concentration. Disconnect the absorber first from the quartz tube and then from the flowmeter. Pour the liquid from the absorber into a 250-ml. conical flask. Pipette 5 ml. of water into the diffuser and force it through into the absorber by means of an aspirator bulb. Repeat three times, adding each washing separately to the conical flask.

[108a] D. Williams, *Ind. Eng. Chem., Anal. Ed., 17,* 295 (1945).

Add 5 ml. of 5 per cent sodium hypochlorite solution to the mixture. Add 8 to 10 ml. of 20 per cent sodium dihydrogen phosphate solution, 200 g. of $NaH_2PO_4.H_2O$ dissolved in water and made to 1 liter. Heat the solution just to boiling. Add 3 to 4 ml. of filtered sodium formate solution, 500 g. of HCOONa dissolved in water and made to 1 liter, and again bring to a boil. Cool to room temperature by holding the flask under the tap. Add 100 ml. of cold (10° C.) water, 2 drops of ammonium molybdate solution containing 50 g. of MoO_3 per liter, 8 to 10 ml. of 30 per cent potassium iodide solution, and 20 to 25 ml. of 6 N sulfuric acid. Titrate promptly with 0.01 N sodium thiosulfate solution. Add 3 to 4 ml. of 1 per cent starch-indicator solution just before the end point is reached and titrate until the last visible trace of pink or blue color just disappears.

A reagent blank containing all the reagents including the 0.1 N sodium hydroxide solution should be prepared and carried through all the operations. The result should be subtracted from the sample titration.

$$\frac{\text{Ml. } 0.010\ N\ Na_2S_2O_3 \times 41.5}{\text{liters of sample}} = \text{ppm. of methyl bromide}$$

The Dudley combustion device, described in the section concerning carbon tetrachloride in this chapter, may also be used for the estimation of methyl bromide in air.

2. *Ethyl Bromide*

Ethyl bromide, monobromoethane, C_2H_5Br, is used as a refrigerant, as an ethylating agent in organic syntheses, as an extraction solvent, and as an anesthetic. It is a colorless inflammable liquid with an ethereal and chloroform-like odor. It boils at 38.4° C. and has a specific gravity of 1.450 at 20/4° C. and a refractive index of 1.4239 at 20° C. Ethyl bromide forms explosive mixtures with air under certain conditions and has a lower limit of inflammability of 6.75 per cent by volume and an upper limit of inflammability of 11.25 per cent.[109] It is readily decomposed into volatile toxic products consisting mainly of hydrobromic acid and bromine in the presence of flames and hot surfaces.

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[109] G. W. Jones, *Ind. Eng. Chem.*, *20*, 367 (1928).

Ethyl bromide is an anesthetic and narcotic. The symptoms produced in guinea pigs when exposed to the vapors of ethyl bromide were similar to those produced by exposure to methyl chloride, ethyl chloride, and methyl bromide.[110] Concentrations of 10–20 per cent by volume were rapidly fatal to guinea pigs. Concentrations of 1–2 per cent were dangerous to the animals for exposures of from 30–60 minutes. The maximum concentration tolerated by the animals for 60 minutes without serious disturbances was 0.6 per cent and the maximum concentrations to which they were exposed for several hours without serious consequences ranged from 0.17 to 0.3 per cent. The generally accepted maximum allowable concentration is 200 parts per million.

Ethyl bromide vapor can be estimated by the explosion-combustion method given for ethyl chloride, the sulfur lamp method on page 589, and other combustion methods.

3. 1,2-Dibromoethane (Ethylene Dibromide)

Ethylene dibromide, *sym*-dibromoethane, $BrCH_2CH_2Br$, 1,2-dibromoethane, is used industrially as a fire extinguisher and in the chemical industry. It is a colorless, heavy liquid with an odor resembling that of chloroform. It boils at 131–132° C. and has a specific gravity of 2.172 at 25/25° C. and a refractive index of 1.5379. One part is soluble in about 250 parts of water and it is miscible with alcohol and ether.

It is a narcotic which is more poisonous than chloroform.

Determination[111,112]

Trap the vapor of ethylene dibromide in an efficient bubbler using alcohol as the trapping agent. The ethylene dibromide may then be estimated by its reaction with potassium iodide with the formation of free iodine, which can be determined by the usual thiosulfate titration. The reaction gives a recovery of only 65.8 per cent when only 1 mg. of ethylene dibromide is present in the reaction mixture and gives 96.9 per cent recovery for 25 mg.

Procedure. Place 10 ml. of 20–30 per cent potassium iodide solution and 50 ml. of alcohol in a 250-ml. flask equipped with a ₸ ground joint.

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[110] R. R. Sayers, W. P. Yant, B. G. H. Thomas, and L. B. Berger, *U. S. Pub. Health Service, Bull. 185* (1929).

[111] W. M. Brenner and G. L. Poland, *Ind. Eng. Chem., Anal. Ed., 10*, 528 (1938).

[112] R. T. Dillon, *J. Am. Chem. Soc., 54*, 952 (1932).

Add an aliquot of the sample to be analyzed. Attach the flask to a water-cooled condenser and reflux for 3 hours. At the end of this period allow the flask to cool and rinse the condenser with a few 10-ml. portions of water. Dilute to a volume of 200 ml. and titrate with standard 0.01 or 0.1 N thiosulfate solution using starch as indicator. Calculate the result from the reaction:

$$C_2H_4Br_2 + 3KI \longrightarrow C_2H_4 + 2KBr + KI_3$$

C. CHLORINE-BROMINE COMPOUNDS

Monobromomonochloromethane

Monobromomonochloromethane, CH_2ClBr, monochloromonobromomethane, is a liquid which has a density of 1.927 at 25° C., a boiling point of 67–68° C., and an index of refraction of 1.4810 at 26° C. A commercial product had a specific gravity of 1.914 at 25° C., a boiling range of 64.8–67.5° C. and an index of refraction of 1.4796 at 25° C. This product has been suggested for incorporation into fire extinguishers.

A study of its toxicity and narcotic action has been made.[113] Monochloromonobromomethane is a narcotic agent of moderate intensity but of prolonged duration. A comparison with carbon tetrachloride shows that monochloromonobromomethane is considerably lower in toxicity.

Its concentration in air may be estimated by modification of the combustion methods described for carbon tetrachloride and by other methods[114] detailed in this chapter.

D. CHLORINE-FLUORINE COMPOUNDS

The principal chlorine-fluorine organic derivatives used in industry are derivatives of methane and ethane. They are used as refrigerants. Among these may be mentioned dichlorodifluoromethane, trichlorofluoromethane, and dichlorotetrafluoroethane.

Dichlorodifluoromethane, CCl_2F_2, known commercially by the trade names of Feron, Kinetic No. 12, and F-12, is a colorless gas which boils at −29.2° C. It has a density of 4.2 referred to air as 1. It is insoluble in water but is soluble in alcohol and ether. It is noncombustible and nonexplosive.

Trichlorofluoromethane, monofluorotrichloromethane, CCl_3F, is known commercially as F-11. It is a colorless liquid which boils at 23.7° C.; has a density of 1.494 at 17.2° C.; and its vapor is 4.8 times as heavy as air. The boiling range of the commercial product extends from 23.6–25.8° C. at 747 mm. of mercury. It is insoluble in water but is soluble in alcohol and ether. It is noncombustible and nonexplosive.

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[113] J. L. Svirbely, B. Highman, W. C. Alford, and W. F. von Oettingen, *J. Ind. Hyg. Toxicol., 29,* 382 (1947).

[114] L. B. Timmis, *J. Soc. Chem. Ind., 63,* 380 (1944).

Dichlorotetrafluoroethane, $C_2Cl_2F_4$, is known commercially as F-114. It is a colorless gas which boils at 4° C. Its vapor density referred to air is 6.0. The commercial product boils in the range 3.6–3.8° C. at 750 mm. mercury. It is insoluble in water but is soluble in alcohol and ether. It, too, is noncombustible and nonexplosive.

Two other chlorine-fluorine organic derivatives are *dichloromonofluoromethane,* $CHCl_2F$, known commercially by the trade name Freon 21, and *monochlorodifluoromethane,* $CHClF_2$ also known as Freon 22.

a. Physiological Response[115]

Dichlorodifluoromethane shows no toxic effects in guinea pigs up to at least 20 per cent by volume for exposures of the order of 2 hours. In tests with concentrations of the order of 28.5–30.4 per cent for exposures of the order of 2 hours, some physiological action, such as nervousness, tremors, and retching movements as well as marked increase in rate and depth of breathing, is apparent, but whether or not this is caused primarily by oxygen deficiency is not shown by the data of Nuckolls. Other investigators[116] also state that the vapor of dichlorodifluoromethane appears to be in a class of practically nontoxic gases.

Trichlorofluoromethane in concentrations of the order of 4.5 to 5.1 per cent for exposures of the order of 2 hours causes guinea pigs to show a marked loss of coordination but they recover rapidly. Concentrations of the order of 10 per cent for an exposure of 2 hours show definite toxic action.

Dichlorotetrafluoroethane in concentrations of 4–5 per cent for an exposure of 2 hours shows no toxic action on guinea pigs. According to Yant, Schrenk, and Patty[117] the toxicity of dichlorotetrafluoroethane on a vapor-volume basis is somewhat greater than dichlorodifluoromethane, but on a weight basis is of the same order as the latter, and it is an organic vapor of remarkably low toxicity.

Dichloromonofluoromethane has been shown to be somewhat more potent than trichloromonofluoromethane. Monochlorodifluoromethane is considered less toxic than trichlorofluoromethane and carbon dioxide but more toxic than dichlorodifluoromethane.

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[115] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

[116] R. R. Sayers, W. P. Yant, J. Chornyak, and H. W. Shoaf, *U. S. Bur. Mines, Rept. Invest., 3013* (1930).

[117] W. P. Yant, H. H. Schrenk, and F. A. Patty, *U. S. Bur. Mines, Rept. Invest., 3185* (1932).

The generally accepted maximum allowable concentration for each of these compounds for an 8-hour daily exposure is 1,000 parts per million.

In the presence of flame and very hot surfaces, around 550° C., dichlorodifluoromethane, trichlorofluoromethane, and dichlorotetrafluoroethane are decomposed with the formation of toxic products such as free chlorine, phosgene, carbon monoxide, hydrochloric acid and hydrofluoric acid, some of which are extremely irritating, and therefore give adequate warning of their presence in air even in very low concentrations.

b. Determination

Chlorofluoroparaffins may be detected by use of the flame detectors described for methyl bromide. Timmis[114] passed the air to be tested over an electrically heated nichrome wire and then tested the decomposition products with Harrison's test paper (page 386) as a means of detecting chlorofluoroparaffins and other halogenated hydrocarbons.

Nuckolls[118] estimated the concentration of chlorine-fluorine compounds of methane and ethane by the vapor-pressure method described on page 559, but this was done for relatively high concentrations. The concentration of these vapors in air may be ascertained by the combustion method described for methyl chloride and by other combustion methods detailed in this chapter.

E. MIXED COMPOUNDS

1. Dichloroethyl Ether

Dichloroethyl ether, *sym-* or β,β'-dichloroethyl ether, known commercially as "Chlorex," is a chlorinated solvent which is principally used as a dewaxing agent for lubricating oils because it is a powerful solvent for the naphthenic components of such oils but is a poor solvent for the paraffin components. In combination with ethyl alcohol it is a solvent for cellulose ester. It is also used as a solvent for fats, tars, oils, and resins. It is used in the textile industry as a cleaning agent, for high-temperature degreasing, and in soaps for scouring, spotting, or fulling. It is also used as a wetting agent and a penetrant. It is finding increasing use as an intermediate in the production of other organic chemicals and as a soil fumigant and insecticide.

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[118] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

Dichloroethyl ether, $ClCH_2CH_2OCH_2CH_2Cl$, is a colorless liquid with a pungent and irritating odor. It boils at 178° C. and has a specific gravity of 1.22 at 20/20° C.; a refractive index of 1.457 at 20° C.; a flash point of 55° C.; and a vapor pressure of approximately 0.73 mm. of mercury at 20° C. It is insoluble in water but is soluble in most organic solvents.

a. Physiological Response

The physiological response of both men and guinea pigs to the vapors of dichloroethyl ether was studied by Schrenk, Patty, and Yant.[119] They found that the physiological action of dichloroethyl ether is primarily irritation of the respiratory passages and the lungs.

> In the order of their appearance, the symptoms produced in guinea pigs were nasal irritation, eye irritation, lachrymation, disturbances in respiration, dyspnea, gasping, and death. All of these appeared in concentrations of 0.026 to 0.10 per cent of the vapor in air. All except lachrymation were attained with 0.01 per cent, while an exposure of 13 hours to a concetration of 0.0035 per cent caused no symptoms other than signs of slight nasal irritation.
>
> At room temperature it was possible to attain a concentration that would be lethal to guinea pigs in a short time. Exposure of the pigs to a concentration of 0.10 per cent for a duration of 30–60 minutes was dangerous to life. The maximum concentration to which the guinea pigs could be exposed for 60 minutes without serious disturbance was 0.01 to 0.02 per cent and the maximum concentration to which they could be exposed for several hours without serious disturbance was 0.0035 per cent by volume.

Concentrations of 0.055 and 0.10 per cent of dichloroethyl ether vapor in air were found to be very irritating to the nasal passages and eyes of men on brief exposure. Lachrymation was profuse and deep inhalations were nauseating. The atmosphere was intolerable. A concentration of 0.026 per cent vapor was similar in effect but to a lesser degree than in the higher concentrations, and though objectionable was not intolerable. A concentration of 0.01 per cent was objectionable because it was slightly nauseating and slightly irritating. A concentration of 0.0035 per cent had an easily noticeable odor which was only slightly offensive and practically free from irritation.

Because of this physiological response in men, the warning properties of dichloroethyl ether are adequate, especially for concentrations which might cause harm in short exposure. The chief danger of this substance lies in exposure to low concentrations for a sufficient length of time to cause marked irritation to the respiratory system.

Comparison with other substances of a poisonous and harmful nature shows dichloroethyl ether to be one of the more toxic compounds. For this reason, the recommended maximum allowable concentration is 15 parts per million.

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[119] H. H. Schrenk, F. A. Patty, and W. P. Yant, *U. S. Pub. Health Service, Reprint 1602* (1933).

b. Detection and Determination

Dichloroethyl ether may be sampled by trapping in efficient bubblers containing saturated alcoholic potassium hydroxide solution. The compound is hydrolyzed by refluxing and the chloride ion produced is estimated by the Volhard method.[120]

Procedure.—Transfer the contents of the bubblers (a series of two is adequate) to an Erlenmeyer flask. Wash the bubblers with small portions of chloride-free saturated alcoholic potash solution and add the washings to the flask. Attach the flask to an efficient reflux condenser and heat for about 2 hours at 100° C. Determine the chloride ion produced after cooling and detaching from the condenser by the Volhard method, as described on page 380.

2. Ethylene Chlorohydrin

Ethylene chlorohydrin, $ClCH_2CH_2OH$, glycol chlorhydrin, monochloroethyl alcohol, is a colorless liquid with a weak odor. The pure material has a specific gravity of 1.200–1.205 at 15° C. and boils at 128° C.; the commercial product, about 96–98 per cent pure, has a specific gravity of 1.198 at 20° C., boils in the range 125–132° C., and has a flash point of 55° C. It is soluble in all proportions in water, alcohol, and benzene and is also soluble in butyl acetate, castor oil, and sulfonated oils. Acetylcellulose is soluble in ethylene chlorohydrin. This substance is a good solvent for acid and basic dyes and for many dye intermediates. It is used industrially for the manufacture of Cellosolve solvents. It is also used as an insecticide and to reduce the dormancy period of seed potatoes. A fatal exposure occurred in 1948 attributable to its use for the latter purpose.

Ethylene chlorohydrin is a compound of high toxicity[121,122] comparable to formaldehyde and hydrogen sulfide. It is readily absorbed through the skin. It is to be noted that rubber gloves offer little protection,[123] since ethylene chlorohydrin can pass through rubber even from aqueous solutions. The recommended maximum concentration is 5 parts of ethylene chlorohydrin by volume per million parts of air.

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[120] H. H. Schrenk, F. A. Patty, and W. P. Yant, *U. S. Pub. Health Repts.*, *48*, 1389 (1933).

[121] H. Dierker and P. G. Brown, *J. Ind. Hyg. Toxicol.*, *26*, 277 (1944).

[122] *Ind. Hyg. Newsletter*, *7*, No. 8, 15 (1947).

[123] H. F. Smyth, Jr., and C. P. Carpenter, *J. Ind. Hyg. Toxicol.*, *27*, 93 (1945).

Determination

The concentration of ethylene chlorohydrin in air may be estimated by absorbing it in potassium hydroxide solution, hydrolyzing it, and determining the amount of chloride ion liberated.

Procedure.—Pass air, at a rate of 1 liter per minute, through two fritted-glass bubblers in series containing a chloride-free, 1 per cent solution of potassium hydroxide. Transfer the absorbent to a flask, reflux for 1 hour, make slightly acid with nitric acid, and titrate the liberated chloride ion with 0.05 *N* silver nitrate solution by the customary Mohr method, using 1 to 2 ml. of 5 per cent potassium chromate solution per 100 ml. of test solution as indicator. One ml. of 0.05 *N* silver nitrate solution is equivalent to 0.0040 g. of ethylene chlorohydrin.

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CHAPTER XVI

Alcohols, Glycols, Alcohol-Ethers, and Ethers

The alcohols, glycols, alcohol-ethers, and ethers are, as in the case with many other organic chemicals, assuming an ever-increasing importance in industry and commerce. These oxygen-containing organic substances are generally more harmful and poisonous than the aliphatic group of hydrocarbons discussed in a previous chapter. Thus all alcohols have a narcotic effect, which is progressively greater with increase in molecular weight. The higher alcohols like butyl and amyl alcohol have in addition an irritant action and possibly some further poisonous action on the protoplasm.[1] The toxicity and potential hazards of the aliphatic alcohols, glycols, and polyhydroxy alcohols have been reviewed by von Oettingen.[1a] The ethers as a group are anesthetic and slightly irritant. The glycols and alcohol-ethers are discussed in their section.

Wherever these liquids and solvents are used industrially, there should be adequate ventilation so as to keep the concentration of their vapors at a minimum.

Among the various purposes for which these substances are employed may be mentioned their use as solvents in the dye, explosive, textile, ink, paint, and varnish industries; as basic materials for the manufacture of other substances, for instance, the manufacture of formaldehyde from methyl alcohol; as antifreeze solutions in water-cooled internal-combustion engines; as germicides, disinfectants, and anesthetics. The wide range of use of these substances contributes to the range in which they are potential health hazards.

A. ALCOHOLS

1. *Methyl Alcohol*

Methyl alcohol is widely used as a solvent for many organic substances, especially in the manufacture and preparation of lacquers, varnishes, pyroxylin plastics, textile soaps, wood stains, and for extraction purposes. It is used, as was mentioned, in the manufacture of formaldehyde, which is the basic material used in the synthesis of formaldehyde-phenol resins, urea-formaldehyde resins, and the like. It is of course one of the materials used for the methylation of other substances and finds an important use as a denaturant for ethyl alcohol. It is used as a component of a mixture with acetone in the fused-collar industry.[2]

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[1] Y. Henderson and H. W. Haggard, *Noxious Gases,* Reinhold, New York, 1927.

[1a] W. F. von Oettingen, *U. S. Pub. Health Service, Bull. 281* (1943).

Methyl alcohol, CH_3OH, also known as methanol and "wood alcohol," is a colorless liquid of pleasant odor. Crude wood spirit has, however, a rather unpleasant odor. It boils at 64.5° C., has a specific gravity of 0.7928 at 20° C. referred to water at 4° C., and a refractive index of 1.33118. Methyl alcohol is miscible in all proportions with water, ethyl alcohol, and ether. It burns in air with a pale blue flame and forms an explosive mixture with air, having a lower explosive limit of 6.7 per cent and an upper explosive limit of 36.5 per cent.

a. Toxicity and Physiological Response

Methyl alcohol is a poisonous substance. It should not be taken internally or applied externally, since systemic poisoning may result from absorption. Prolonged inhalation should be avoided. Adequate ventilation should be provided wherever it is used. It has a particular effect on the optic nerve and the ingestion or inhalation of a sufficient quantity of this substance may cause blindness and even death. The symptoms exhibited in less severe cases of poisoning are headache, nausea, vomiting, and irritation of the mucous membranes. More severe poisonings show signs of convulsions, cyanosis, paralysis, and visual hallucinations. The generally accepted maximum allowable concentration[3] for daily 8-hour exposures is 200 parts of methanol per million parts of air by volume, corresponding to 0.26 mg. per liter at 25° C. and 760 mm.

b. Detection

Schiff's Test. An atmosphere suspected of containing methyl alcohol may be sampled by drawing the air through a bubbler or trap containing water. This water sample is oxidized to formaldehyde, which is in turn detected with fuchsin-sulfite solution, that is, Schiff reagent. The air may also be sampled by passing it directly through 5 per cent alkaline permanganate solution.

Preparation of Schiff Reagent. Dissolve 0.5 g. of pure fuchsin in 400 ml. of warm water. Cool, add 2 g. of anhydrous sodium bisulfite, and stir till dissolved. Add 4 ml. of concentrated sulfuric acid. Transfer to a brown bottle and allow to stand at least overnight before use. This reagent will not deteriorate over long periods if kept in a refrigerator.

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[2] L. Greenburg, M. D. Mayers, L. Goldwater, and W. J. Burke, *J. Ind. Hyg. Toxicol.*, *20,* 148 (1938).

[3] *Am. Standards*, Z37.14–1944.

As a check, a test for formaldehyde should be made on a portion of the sample before oxidation with permanganate. This colorimetric test for methyl alcohol should be interpreted with caution if other materials that are likely to give formaldehyde on oxidation with permanganate are present, for instance glycerol or pectin.

Procedure. Transfer 0.5 ml. of the sample to a test tube and dilute with 4.5 ml. of water. Add 2 ml. of a freshly prepared aqueous solution containing 3 g. of potassium permanganate and 15 ml. of phosphoric acid per 100 ml. Allow the mixture to stand for 10 minutes. Add 2 ml. of a solution containing 5 g. of oxalic acid dissolved in 100 ml. of a cooled mixture of equal volumes of sulfuric acid and water. When the test solution is decolorized, add 5 ml. of the Schiff reagent prepared as directed above and mix well. Allow to stand for 10 minutes. The presence of methyl alcohol is indicated by the production of a blue or violet color. No other aldehydes interfere because the production of color by other aldehydes is inhibited by the addition of acid.

Rosaniline Modification.[4] The rosaniline modification of the Schiff test is a method which also depends on the oxidation of methanol with permanganate to form formaldehyde but the formaldehyde is detected in turn by the use of a reduced rosaniline solution.

Reagents. (1) Modified Schiff's Reagent.—Dissolve 0.2 g. of rosaniline or an equivalent weight of its salt in 120 ml. of hot water, cool, and add this to a solution of 2 g. of sodium bisulfite in 20 ml. of water. Finally add 2 ml. of concentrated hydrochloric acid and dilute the entire mixture to 200 ml. This solution should become colorless or nearly so after standing. If it is protected from the air, no deterioration results.

(2) Potassium Permanganate.—Dissolve 3 g. of potassium permanganate in 100 ml. of water, previously distilled over potasium permanganate, and containing 15 ml. of phosphoric acid. By using water previously distilled from potassium permanganate solution, this reagent can be kept for a long time.

(3) Oxalic Acid Solution.—Dissolve 5 g. of oxalic acid in a solution made by diluting 50 ml. of sulfuric acid, specific gravity 1.84, to 100 ml. with water.

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[4] L. O. Wright, *Ind. Eng. Chem., 19,* 750 (1927).

Procedure.[5-7] Place 2 ml. of the collected sample in a test tube and add 1 ml. of potassium permanganate solution. Allow to stand for 10 minutes. Decolorize by adding 1 ml. of the oxalic acid solution, followed by 2 ml. of the modified Schiff's reagent, and mix. The solution must be mixed thoroughly. If methanol is present a violet color is developed. With traces of methanol the color is not developed for an hour.

Glycerol in sufficient amounts will produce a like reaction and color and for that reason where glycerol is suspected in the collected air sample, the test should be repeated on a distillate obtained from the collected air sample.

Chromotropic Acid Test. The U. S. P. XII test for the detection of methyl alcohol in whiskey may be modified for the detection of this substance in air. To 1 drop of the bubbler solution or of a distillate, add 1 drop of 5 per cent phosphoric acid and 1 drop of 5 per cent potassium permanganate solution. Mix, allow to stand for 1 minute, and add 5 per cent sodium bisulfite solution dropwise until the permanganate color is discharged. If a brown color remains add an additional drop of phosphoric acid. To the colorless solution add 5 ml. of freshly prepared chromotropic acid solution, prepared by dissolving 50 mg. of chromotropic acid, 1,8-dihydroxynaphthalene-3,6-disulfonic acid, or its sodium salt in 100 ml. of 75 per cent sulfuric acid, and heat in a water bath for 10 minutes at 60° C.

c. Quantitative Estimation

Methyl alcohol may be quantitatively determined by a modification of the Schiff test.[8] Transfer 10 ml. of the methyl alcohol solution, trapped by bubbling a known volume of air through a series of absorption devices, to a 25-ml. volumetric flask and add 1 ml. of 5 per cent ethyl alcohol by volume. Add 1 ml. of 1 per cent potassium permanganate solution and then 1 ml. of phosphoric acid solution, 25 ml. of 85 per cent phosphoric acid in 100 ml. of water. Allow the mixture to stand for 1 hour with occasional shaking. Add 1 ml. of 5 per cent oxalic acid solution. When the mixture is colorless, add 2 ml. of sulfuric acid solution, 30 ml. concentrated sulfuric acid in 100 ml. of water. Then add 5 ml. of the Schiff reagent. Mix by inverting the flask. After 3 hours compare in a colorimeter against a standard treated exactly the same way at the same time.

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[5] R. M. Chapin, *Ind. Eng. Chem.*, *13*, 543 (1921).

[6] E. Elvove, *Ind. Eng. Chem.*, *9*, 295 (1917).

[7] G. Deniges, *Compt. rend.*, *150*, 823 (1910).

[8] C. M. Jephcott, *Analyst*, *60*, 588 (1935).

This method holds for 0.3 mg. in 10 ml. of test solution, that is, for 30 parts per million, although 0.05 mg. in 10 ml. (5 parts per million) may be detected qualitatively. The color produced is not strictly proportional to the concentration. However, in the range from 1 mg. per 10 ml. to 2.5 mg. per 10 ml. (100 parts per million to 250 parts per million), the color is apparently a straight-line function of the concentration. Consequently it is best to keep quantitative determinations within this range.

It is to be noted that methyl alcohol is estimated in the presence of ethyl alcohol in this method.

Ackerbauer-Lebowich Modification.[9] In this modification both methanol and formaldehyde are estimated. Three simple absorbers are arranged in series and connected to a 5- or 10-liter aspirator bottle. The inlet tubes of the absorbers are adjusted to an orifice of 1.6 mm. The first absorber contains a mixture of 75 ml. of 2 per cent phosphoric acid and 75 ml. of 4 per cent barium chloride solution to give 150 ml. of 1 per cent phosphoric acid and 2 per cent of barium chloride solution, respectively. The contents of this absorber may be used for about 10 determinations. The second solution contains 200 ml. of an alkaline 5 per cent potassium permanganate solution and the third absorber contains 225 ml. of modified Schiff's reagent (page 615). A fourth absorber containing 200 ml. of 2 *N* sodium bisulfite solution may be used to trap any formaldehyde escaping from the third absorber. In general, this will be negligible, hence the fourth absorber need not be used.

In the first absorber, carbon dioxide, sulfur dioxide, chlorine, and like interferences are trapped. The entrainment of formaldehyde is about 1 part per thousand. Methyl alcohol is trapped and oxidized in the second absorber, while in the third absorber over 97 per cent of the formaldehyde reacts with the rosaniline reagent.

Decolorize the solution in the second absorber with oxalic and sulfuric acids as detailed above, add rosaniline-sulfite reagent, and compare the color obtained visually with standards. Compare the color obtained in the third absorber visually also.

2. *Ethyl Alcohol*

Ethyl alcohol is universally used in industry as a solvent. It is a component of a vast number of mixtures and solutions of a pharmaceutical nature. It is a solvent for resins and many organic and inorganic chemicals. It is used in the manufacture of pyroxylin and other plastics, the manufacture of vinegar, rayon, ethyl ether, esters, acetic acid, and many other organic chemicals. It is used as a diluent in shellac, varnishes, lacquers, and enamels. It is used as a liquid fuel. It is a component of cosmetic and toilet preparations, antiseptics, and disinfectants. The production of synthetic drugs, dyestuffs, cleansers, lubricants, and a host of other materials and products requires the use of a large amount of this solvent.

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[9] C. F. Ackerbauer and R. J. Lebowich, *J. Lab. Clin. Med., 28,* 372 (1942).

Probably the most common point of contact of ethyl alcohol and man is not in industrial applications but as the alcoholic beverages, whiskey, wine, and beer.

Stringent government regulations cover the manufacture, use, and sale of ethyl alcohol in all forms. Alcohol not for beverage purposes is tax-free. However, such tax-free alcohol is either used under direct governmental supervision or, after being completely or specially denatured so as to render it unfit for beverage purposes, is used without direct supervision. The use of all alcohol, whether tax-paid, tax-free, or specially or completely denatured, must be accounted for by records.

Ethyl alcohol, CH_3CH_2OH, is a colorless liquid with a pleasant odor and a burning taste. It boils at 78.5° C., and when distilled with water will form a constant minimum boiling point for the mixture of 78.15° C. consisting of 95.6 per cent of alcohol and 4.4 per cent of water. Its density is 0.7893 at 20° C. referred to water at 4° C. It has a refractive index of 1.361 at 20° C. Ethyl alcohol is designated as "alcohol," in contradistinction to all other alcohols, which must be specifically named. Anhydrous ethyl alcohol is termed "absolute" alcohol.

Ethyl alcohol is miscible with water and ethyl ether in all proportions and, as its vast use in industry indicates, is capable of dissolving a great many substances. When ignited it burns in air with a pale-blue, transparent flame with the formation of carbon dioxide and water. The vapor forms an explosive mixture with air.

a. Toxicity and Physiological Response

The intoxicating effect of alcoholic beverages became a matter of national importance a generation ago and the alcoholic-liquor prohibition amendment was added to the Constitution of the United States in 1919, as Article XVIII. Its importance did not diminish with the succeeding years and Article XVIII was repealed by a subsequent amendment, Article XXI. The agent that produces the intoxicating effect of alcoholic beverages is ethyl alcohol. In the human body the principal action of ethyl alcohol is that of a mental depressant, not a stimulant, as is commonly believed. In moderate doses, well-diluted alcohol stimulates the appetite, induces secretion of gastric juice, and aids in the absorption of food. When ingested repeatedly in stronger forms than mild alcoholic beverages, alcohol is an irritant to the mucous membrane lining of the stomach. When ethyl alcohol is taken to excess it is particularly toxic to the nervous system, paralyzing the respiratory center, and is a direct and principal cause of several kinds of mental disease. When inhaled it acts principally as a narcotic. The generally recommended maximum allowable concentration for a daily 8-hour exposure to ethyl alcohol is 1,000 parts per million.

b. Detection

In order to detect the presence of alcohol vapor in air, the air should be passed through some trapping device containing water at a rate of about 20 liters per hour. This sample can then be transferred to a volumetric flask, made to volume with water washings of the bubbler, and aliquots can be withdrawn for qualitative and quantitative estimation. Small amounts of alcohol can be detected by means of the iodoform test and the ethyl benzoate test.

Iodoform Test. To 5 ml. of the sample add 10 drops of 10 per cent sodium hydroxide solution and then add a solution of iodine in potassium iodide drop by drop until a faint permanent yellow color is obtained, showing the presence of a slight excess of iodine. Allow the solution to stand for several minutes, shake, and note the formation of crystals or the odor of iodoform. If no positive result is obtained in the cold, heat the tube to 60° C. for 1 minute and again allow to stand. A yellow crystalline precipitate of iodoform indicates the presence of ethyl alcohol. This reaction is not specific for ethyl alcohol for it is given by a number of substances having the $CH_3.CH(OH).C$ or $CH_3.CO.C$ groups. Thus, for instance, acetone and lactic acid give the same reaction.

Ethyl Benzoate Test. To another 5 ml. portion of the sample add a few drops of benzoyl chloride and a few ml. of 10 per cent sodium hydroxide solution, and warm. The formation of ethyl benzoate with its characteristic fruity odor confirms the presence of ethyl alcohol. Acetone and lactic acid do not give this reaction. On the other hand, methyl alcohol, which also forms a characteristic fruity-smelling compound with benzoyl chloride, does not give the iodoform test.

Xanthogenate Reaction. This is a general reaction of the alcohols.

Place 1 drop of the sample into a small test tube. Add 1 drop of carbon disulfide and a piece of a pellet of sodium hydroxide and shake. Allow the pellet to dissolve and acidify to litmus with dilute sulfuric acid. Shake out with 2 drops of chloroform. A violet color in the chloroform layer indicates the presence of an alcohol.

c. Quantitative Estimation

When the presence of alcohol has been qualitatively demonstrated and sufficient air has been sampled by passage through the bubbler to provide a 0.1 per cent by volume aqueous solution of alcohol, the quantity of alcohol present can be determined by obtaining the specific gravity of the solution with the aid of a pycnometer. This will be accurate provided there are no other absorbable components in the air to alter the specific gravity of the water, for instance methyl or other alcohol homologues, or volatile acids like acetic acid. If sufficient air is sampled to yield more than a 0.5 per cent by volume aqueous solution of alcohol, the quantity present can be estimated by use of the immersion refractometer.

If other absorbable components are present, such as a volatile acid, which can be separated from ethyl alcohol by distillation, the water sample, after neutralization with alkali, can be distilled and the specific gravity and refractive index of the distillate can be used to ascertain the quantity of alcohol present in the air.

Most of the ethyl alcohol used as a solvent, etc., in industrial processes is completely or specially denatured with substances which are themselves volatile and which are often far more poisonous than ethyl alcohol itself. It is clear that in these instances not only the alcohol but the denaturant itself is likely to be a contaminant of the atmosphere. The most widely used denaturant is methyl alcohol or wood spirit. Where only small quantities of methyl alcohol are present along with ethyl alcohol, the quantity of methyl alcohol present is preferably estimated colorimetrically, as described above. Where sufficient methyl and ethyl alcohols have been collected by means of long sampling or because of high concentration, the amount of methyl and ethyl alcohols can be estimated by use of the principle that methyl alcohol decreases the refraction of ethyl alcohol in direct proportion to the amount of methyl alcohol present. The reader is referred to Herstein and Jacobs[10] or the *Methods of the A. O. A. C.*[11]

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[10] K. Herstein and Morris B. Jacobs, *Chemistry and Technology of Wines and Liquors.* Van Nostrand, New York, 1948.

[11] *Methods Assoc. Official Agr. Chemists* (6th ed.), 1945.

The concentration of ethyl alcohol in air may be estimated by the general adsorption methods detailed in Chapter XII, by oxidation with iodine pentoxide with subsequent titration of the hydriodic acid and iodine liberated,[12,13] and by other oxidation methods. Alcohol can be conveniently sampled in a bubbler containing 1.5 per cent potassium chromate in 1:1 sulfuric acid or in a mixture of 5 ml. of 0.3472 *N* potassium dichromate plus 5 ml. of concentrated sulfuric acid, as mentioned below.

Nicloux Method. Ethyl alcohol can be estimated by oxidation to acetic acid with dichromate solution:

$$3C_2H_5OH + 2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3CH_3COOH + 11H_2O$$

Then either the acetic acid formed is determined by distillation and subsequent titration of the distillate[14]; or the excess dichromate is estimated iodometrically.[15]

Reagent. Potassium Dichromate Solution.—Dissolve 17.042 g. of pure, dry potassium dichromate, $K_2Cr_2O_7$, in water and dilute to 1 liter in a volumetric flask. This is a 0.3472 *N* solution, each ml. of which can oxidize 4 mg. of ethyl alcohol to acetic acid.

Procedure. Transfer, with a pipette, an aliquot of the bubbler sample containing not more than 10 mg. of alcohol to a large test tube, 20 cm. by 25 mm. in diameter. Pipette a 5-ml. aliquot of the 0.3472 *N* potassium dichromate solution into the tube. Mix thoroughly and add 5 ml. of concentrated sulfuric acid with a protected pipette while continuously shaking the tube. Place in a boiling-water bath for 15 minutes to complete the oxidation to acetic acid. Cool the tube and pour the contents into a 500-ml. glass-stoppered bottle or iodine flask containing 250 ml. of cold water. Stir well, add 3 g. of potassium iodide, and after 5 minutes standing, titrate the liberated iodine with 0.05 *N* thiosulfate solution, using 1 per cent starch solution as the indicator.

Run a blank determination, carrying out all the operations and reagents, using the same volume of water instead of the aliquot of the test solution. The difference in the sodium thiosulfate titrations is equivalent to the number of ml. of dichromate solution used by the alcohol,

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[12] H. W. Haggard and L. A. Greenberg, *J. Pharmacol. Exptl. Therap.*, *52*, 137 (1934).

[13] L. A. Greenberg and F. W. Keator, *Quart. J. Studies Alc.*, *2*, 57 (1941).

[14] A. O. Gettler and A. Tiber, *Arch. Path.*, *3*, 75 (1927).

[15] W. D. McNally, *Toxicology*, Industrial Medicine, Chicago, 1937.

the weight of which can be gained from the equivalent factor given above.

McNally[15] describes a method in which methyl and ethyl alcohol can be determined in the presence of one another by means of oxidation with dichromate. The mixed alcohols are oxidized by 2 per cent potassium dichromate solution in the presence of concentrated sulfuric acid. The carbon dioxide formed in the reaction

$$CH_3OH + K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow CO_2 + K_2SO_4 + Cr_2(SO_4)_3 + 6H_2O$$

is absorbed in weighed tubes containing Ascarite and Dehydrite, the amount of methyl alcohol being obtained from the increase in weight. The ethyl alcohol present is obtained by distilling the acetic acid formed and titrating the distillate. Corrections are applied for the amount of ethyl alcohol oxidized to carbon dioxide.

Titrimetric Method.[15a] Ethyl alcohol may be estimated by oxidation with a standard solution of potassium dichromate in sulfuric acid, the excess being estimated titrimetrically.

Place 25 ml. of a mixture consisting of 100 ml. of 0.5 *N* potassium dichromate solution, 100 ml. of concentrated sulfuric acid and 50 ml. of water into an absorption flask. Draw a known volume of air through the device.

Transfer the test mixture quantitatively to a ₮ flask equipped with a reflux condenser, dilute to 70 ml., boil under the reflux for 15 minutes, and allow to cool. Add 100 ml. of 2 per cent sodium iodide solution and titrate the liberated iodine with standard sodium thiosulfate solution, using starch solution as indicator. One ml. of thiosulfate is equivalent to 0.00115 g. of alcohol. Run a blank determination as a control.

The alcohol may also be adsorbed on activated carbon. It may subsequently be liberated from the carbon by distillation and the alcohol in the distillate may be estimated as detailed above.

Determination of Small Amounts of Ethyl and Methyl Alcohols.[16] The method is based upon the reduction of potassium permanganate by the two alcohols, the quantity of each in the mixture being calculated from the difference in amount of potassium permanganate reduced in alkaline and in acid solution respectively. In alkaline solution methyl alcohol is oxidized by potassium permanganate to carbon dioxide and water, whereas ethyl alcohol forms varying amounts of acetic acid and oxalic acid, depending upon temperature conditions and the like. In phosphoric acid solution, potassium permanganate oxidizes methyl alcohol to carbon dioxide and water and ethyl alcohol to acetic acid and water. By controlling the excess permanganate, the temperature, and the dilution of the test solution, ethyl alcohol can be made to reduce the same amount of permanganate as an equal weight of methyl alcohol.

[15a] Elliott and J. Dalton, *Analyst*, *44*, 132 (1919)

[16] O. Hepter, *Z. Nahr.-Genussm.*, *26*, 342 (1913).

Reagent. Alkaline Potassium Permanganate Solution.—Dissolve 16 g. of potassium permanganate, $KMnO_4$, and 40 g. of sodium hydroxide in water and dilute to 1 liter. This is approximately half normal. Standardize against 0.5 *N* oxalic acid solution.

Procedure. A preliminary determination is made to ascertain the approximate strength of the alcohol mixture. Dilute 25 ml. of the 0.5 *N* alkaline permanganate solution with 50 ml. of water, heating for 5–10 minutes on a water bath and adding little by little with the aid of a burette sufficient of the alcohol solution to impart a deep-green color to the mixture.

Continue heating for 15–20 minutes, add 25 ml. of 0.5 *N* oxalic acid, containing 60 ml. of concentrated sulfuric acid per liter, to the mixture. Titrate back with 0.5 *N* acid potassium permanganate solution, containing 16 g. of $KMnO_4$ and 40 g. of crystalline phosphoric acid, H_3PO_4, per liter. One ml. of 0.5 *N* permanganate solution represents about 0.0025 g. of alcohol.

Dilute the alcohol solution to 0.1–0.25 per cent by weight. Measure 25 ml. of 0.5 *N* alkaline permanganate solution into a 200-ml. flask, dilute with water to about 80 ml., warm to 30–40° C., add sufficient of the alcohol solution to represent 0.025 g. of total alcohol, and immediately place the mixture, which should now have a temperature of about 25° C. and a volume of about 100 ml., on the steam bath, where it should attain a temperature of 92–94° C. within 6 minutes. This temperature is maintained for 15–20 minutes. Add 25 ml. of 0.5 *N* oxalic acid to the hot mixture and titrate back with 0.5 *N* acid permanganate solution. The volume of alkaline permanganate reduced should not be less than 7 ml. nor more than 12 ml.

The results are calculated from the following formulas:

$$p = \frac{0.2667v_1}{n_1}$$

$$x = \left(\frac{50v_2}{n_2p}\right) - 87$$

$$y = \frac{px}{100}$$

$$z = p - \left(\frac{px}{100}\right)$$

where: p = grams total alcohol per 100 ml.
x = grams methyl alcohol per 100 g. of total alcohol
y = methyl alcohol per 100 ml.
z = ethyl alcohol per 100 ml.
n_1 = ml. of alcohol solution used in the alkaline permanganate reduction
n_2 = ml. of alcohol solution used in the acid permanganate reduction
v_1 = ml. of 0.5 *N* alkaline permanganate solution used in the alkaline treatment
v_2 = ml. of 0.5 *N* acid permanganate used in the acid reduction

All the results are referred to the solution after dilution to 0.1–0.25 per cent of alcohol by weight.

Acetyl Value. Compounds containing a hydroxyl group can be esterified with acetic anhydride with the formation of the ester and free acetic acid:

$$C_2H_5OH + (CH_3CO)_2O \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

After neutralization the mixture is saponified and the excess alkali is determined by titration. The *acetyl value* is defined as the number of milligrams of potassium hydroxide required to combine with the acetic acid liberated from 1 g. of acetylated substance.

Procedure. Heat about 0.5 g. of the hydroxyl compound under a reflux condenser on a steam bath with about 1 ml. of acetic anhydride. Cool the solution, dilute with water, warm to about 50° C., and keep at this temperature for a short time. Neutralize the mixture to phenolphthalein. Add a measured quantity of 1 *N* alcoholic potassium hydroxide and saponify by heating under a reflux condenser. Titrate the excess alkali with standard acid. Run a blank determination on the same volume of the standard alcoholic potash solution. The difference is the number of ml. of standard potassium hydroxide used by the acetylated compound in the saponification.

Acetyl Values of Alcohols

Substance		Substance	
Amyl alcohol	636	Glycerol	772
Butyl alcohol	758	Methyl alcohol	1,753
Cyclohexanol	492	Methylcyclohexanol	492
Ethyl alcohol	1,219	Propyl alcohol	935

Determination of Ethyl and Butyl Alcohol in Mixtures.[17] This method depends upon the oxidation of ethyl and butyl alcohols to acetic and butyric acids, respectively, by dichromate and the subsequent separation of the fatty acids by means of isopropyl ether.

Adjust the neutrality of the aqueous mixture and distill over one-half to two-thirds of the mixture. Precipitate compounds containing the carbonyl group, such as acetone, acetoin (acetyl methyl carbinol), or acetaldehyde, by use of 2,4-dinitrophenylhydrazine and redistill the alcohols from an alkaline solution. Transfer 50 ml. of the distillate to a 200-ml. round-bottom flask, and add 10 g. of potassium dichromate and 25 ml. of 85 per cent phosphoric acid. Attach the flask to a reflux condenser, bring to a gentle boil in 1.5 minutes, and maintain boiling for an additional 3 minutes. Wash the condenser with 5 ml. of water through the top. Do not allow the volume of liquid in the oxidation flask to exceed 100 ml.

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[17] C. H. Werkman and O. L. Osburn, *J. Bact.*, *21*, 20 (1931).

Connect the oxidation flask to a distillation condenser and distill, catching the distillate in a 100-ml. volumetric flask, until the mixture in the flask begins to foam. Lower the heat and continue the distillation with slight foaming for 2 to 3 minutes more. This will avoid entrainment of phosphoric acid. Make up to volume and determine the total acid in a 25-ml. aliquot by titration with standard alkali solution. Express the results in ml. of 0.1 N acid. Partition 30 ml. by the isopropyl ether method.[18]

Under the conditions given above, ethyl alcohol is oxidized quantitatively to acetic acid, while 90 per cent of the butyl alcohol is oxidized to butyric acid and the remaining 10 per cent to acetic acid. The percentage of butyric acid actually found may be read from the Werkman nomogram. This percentage divided by the 0.9 factor and multiplied by the number of ml. of 0.1 N acid found in the sample distillate gives the amount of acid attributable to the butyl alcohol. This in turn is equivalent to the amount of 0.1 N butyl alcohol that may be considered to be present in the original mixture. The difference between this result and the total amount of acid found is the amount representing 0.1 N ethyl alcohol.

For example, assume that the distillate contains 100 ml. of 0.1 N acid. The partition constant is 16.5. This is equivalent to a mixture containing 60 per cent butyric acid and 40 per cent acetic acid. Then $0.60/0.9 \times 100 = 66.6$ ml. of 0.1 N acid = 66.6 ml. of 0.1 N butyl alcohol, and $100 - 66.6 = 33.4$ ml. of 0.1 N ethyl alcohol. The original 50 ml. taken for oxidation contained 0.4928 g. of anhydrous butyl alcohol and 0.1536 g. of anhydrous ethyl alcohol.

3. Allyl Alcohol

Allyl alcohol, $CH_2{:}CHCH_2OH$, is a colorless mobile liquid with a characteristic pungent odor. It has a density of 0.8535 at 20° C.; it boils at 96.9° C.; it has a refractive index of 1.4133 at 20° C.; its flash point, open cup, is 90° F.; and its lower and upper limits of inflammability in air are 2.5 and 18.0 per cent by volume, respectively. Allyl alcohol is miscible with water and forms a constant boiling mixture at 88.9° C. containing 72.3 per cent allyl alcohol by weight. It is miscible with all the common organic solvents. Allyl alcohol is used for the manufacture of many organic chemicals.

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[18] C. H. Werkman, *Ind. Eng. Chem., Anal. Ed.*, *2*, 302 (1930).

Allyl alcohol is a toxic material, with fairly adequate warning properties.[19] Its vapors are irritating to the eyes, nose, and throat. It is readily absorbed through the skin, hence precautions must be observed to avoid contact with this material and thus avoid burns and internal injury. A maximum allowable concentration of 15 parts per million has been suggested for this compound in California.

Because allyl alcohol is both an unsaturated compound and an alcohol, it undergoes many reactions. Some of these can be adapted for its determination in air. Very small amounts may be detected and estimated by trapping the allyl alcohol in water or sulfuric acid and oxidizing it with chromic-sulfuric acid to acrolein. The latter may then be determined by the methods detailed on page 680. Allyl alcohol also gives a cherry-red color when treated with a 1 per cent solution of vanillin in concentrated sulfuric acid. Allyl alcohol also reacts with some phenols and alkaloids to give colored compounds.

4. *Isopropyl and n-Butyl Alcohols*

Isopropyl and *n*-butyl alcohols are homologues of methyl and ethyl alcohol. They are used extensively as solvents or diluents for the manufacture and preparation of many materials. Among these uses may be mentioned airplane dopes, lacquers, plastics, safety glass, perfumes, cosmetics, paint and varnish removers, and as denaturants for ethyl alcohol.

Butanol is used in industry not so much because of its own solvent power but because it has the ability of making other substances soluble in each other. For instance, about 5 per cent of *n*-butyl alcohol will permit such immiscible liquids as alcohol and benzine to mix together. The apparent solubility of cellulose nitrate in butyl acetate is increased by the addition of *n*-butanol.

Isopropyl alcohol, $CH_3CHOHCH_3$, isopropanol, is a colorless liquid with a pleasant characteristic odor resembling acetone. Its specific gravity is 0.79 at 20/20° C. and it boils at 82.4° C. Its refractive index is 1.3780 at 20° C. It is soluble in water in all proportions and forms a constant boiling mixture containing approximately 91 per cent of isopropyl alcohol and 9 per cent of water by volume. This mixture boils at 80.3° C.

n-Butyl alcohol, $CH_3CH_2CH_2CH_2OH$, *n*-butanol, is a colorless liquid with a characteristic odor faintly resembling that of isoamyl alcohol. It has a specific gravity ranging from 0.810 to 0.813 at 20/20° C. depending upon its purity. It boils in the range of 115–118° C. and has a refractive index of 1.3993 at 20° C. It burns with a luminous flame. It is soluble in water, forming an 8.9 per cent solution by volume at 25° C., and will itself dissolve 17.1 per cent by volume of water at the same temperature. It forms a constant boiling mixture with water, which contains 63 per cent by weight of butanol and boils at 92.3° C.

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[19] *Allyl Alcohol,* Shell Chem. Corp., New York.

a. Physiological Response

All alcohols, as has been previously mentioned, are slightly narcotic. Isopropyl alcohol is not considered particularly toxic and resembles in some measure ethyl alcohol in its physiological response. The maximum allowable concentration is 400 parts per million.

The vapors of butyl alcohol have an irritant effect and cause coughing, in a manner similar to amyl alcohol, but of less intensity. Butyl alcohol in concentrations of 100 parts per million has caused damage to the blood, liver, and kidneys of experimental animals.[20] It is also known that butyl alcohol causes marked dermatitis, early liver degeneration, and a definite increase in red blood cells. Smyth and Smyth[21] studied the effects of *n*-butanol and Tabershaw and co-workers[22] found that over 50 parts per million may cause eye inflammation. The recommended maximum allowable concentration for an 8-hour daily exposure is 50 parts of *n*-butanol per million parts of air by volume.

b. Detection and Estimation of Isopropyl Alcohol

Deniges Reaction. To 2 ml. of the sample solution, obtained by trapping the vapors in water in efficient bubblers, add 3 ml. of water and 10 ml. of a solution of mercuric sulfate, made by dissolving 5 g. of yellow mercuric oxide by mixing the oxide with 40 ml. of water, adding 20 ml. of concentrated sulfuric acid, and then adding another 40 ml. of water and stirring until completely dissolved. Heat the mixture on a boiling-water bath for 3 minutes. A precipitate indicates the possible presence of isopropyl alcohol. Acetone, other ketones, and tertiary butyl alcohol also give this reaction.

In the absence of acetone, isopropyl alcohol may be confirmed by the following test. Place 8 g. of chromic acid, CrO_3, in a Kohlrausch flask of about 100 ml. capacity or some other suitable flask and add 15 ml. of water and about 2 ml. of concentrated sulfuric acid. Connect the flask with a reflux condenser and add very slowly through the condenser 5 ml. of the sample to be tested. The reaction is very vigorous and causes the solution to boil. Continue boiling under the reflux condenser for about $^1/_2$ hour; cool and distill, without transferring the liquid, until 2 ml. have been collected, using a 10-ml. graduated cylinder as a receiver. Mix the distillate and test for acetone as above with Deniges reagent, using, however, 2 ml. of Deniges reagent and not more than 4 to 5 drops of the distillate. Bring to a boil, keeping the solution at just about boiling temperature about 1 minute or slightly longer. A fine white precipitate that does not settle rapidly is indicative of acetone, which was obtained from the oxidation of isopropyl alcohol. Any precipitate formed after heating 2 minutes and allowed to cool should be disregarded. Acetaldehyde, paraldehyde, ethyl acetate, acetic acid, and mixtures of these do not interfere.

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[20] W. J. Burke and L. Goldwater, *N. Y. State Ind. Bull. 17*, 314 (1938).

[21] H. F. Smyth and H. F. Smyth, Jr., *J. Ind. Hyg., 10*, 261 (1928).

[22] I. R. Tabershaw, J. P. Fahy, and J. B. Skinner, *J. Ind. Hyg. Toxicol., 26*, 328 (1944).

In case acetone is present it may be estimated quantitatively as described on page 685, using an aliquot of the sample. In another aliquot, the isopropyl alcohol is oxidized to acetone and the total acetone is determined. From the difference, the amount of isopropyl alcohol present may be computed. It has been found that only 94 per cent of isopropyl alcohol is quantitatively oxidized to acetone.

Sodium Nitroprusside Test. This test[23,24] also depends on the oxidation of isopropyl alcohol to acetone. Transfer 10 ml. of the sample to a distillation flask and add 20 ml. of 1 per cent potassium dichromate solution and 1 ml. of concentrated sulfuric acid. Distill until 3 ml. of distillate have been collected. Place a mixture of 2 ml. of 5 per cent sodium nitroprusside solution, 2 ml. of concentrated ammonium hydroxide solution, and 0.3 g. of ammonium chloride in a test tube. Overlay with the 3 ml. of distillate. In the presence of acetone a purple ring is formed at the interface. This test will detect about 100 mg. of isopropyl alcohol in 10 ml. of sample.

As an alternative method of determining isopropyl alcohol in air, it may be adsorbed on silica gel,[24a] liberated by steam distillation, converted to isopropyl nitrite, and then estimated after liberation of nitrous acid titrimetrically by the method of Knipping and Ponndorf.[24b]

c. Determination of Butyl Alcohol

The concentration of *n*-butyl alcohol in air may be estimated by the general methods for solvents such as adsorption methods and combustible indicator methods. The general methods for the determination of alcohols may also be employed. A method for its determination in mixtures by

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[23] J. Rae, *Pharm. J., 116,* 630 (1926).

[24] E. C. Wagner, *J. Chem. Education, 11,* 309 (1934).

[24a] E. Hahn, *Biochem. Z., 292,* 148 (1937).

[24b] H. W. Knipping and W. Ponndorf, *Z. physiol. Chem., 160,* 25 (1926).

oxidation to butyric and acetic acids has been detailed in the discussion concerning ethyl alcohol.

The Nicloux method may be used for its estimation. This method has been detailed for ethyl alcohol. When *n*-butyl alcohol is oxidized by dichromate under the conditions detailed by Werkman,[17,18] 90 per cent is converted to butyric acid and 10 per cent to acetic acid. The excess dichromate may be estimated iodometrically. This method has been used by Tabershaw, Fahy, and Skinner.[22]

A method for the estimation of *n*-butyl alcohol in the presence of ethyl alcohol and acetone is detailed by Christensen and Fulmer.[24c]

Isobutyl alcohol may be estimated by the general methods for solvents previously detailed. It is oxidized by dichromate to an aldehyde. The latter may be detected by the use of *o*-nitrobenzaldehyde, with which it gives a color reaction.[24d]

5. Amyl Alcohol and Isoamyl Alcohol

Isoamyl alcohol, isobutyl carbinol, is the most common of the isomeric amyl alcohols, of which eight are known. It is used extensively in lacquers, varnishes, in the manufacture of synthetic rubber, in the preparation of esters, and as a solvent for dyes, oils, and waxes.

Isoamyl alcohol, $(CH_3)_2CHCH_2CH_2OH$, is a colorless liquid with an unpleasant irritating odor. It has a specific gravity of 0.813 at 15/4° C. The specific gravity of the commercial product is nearer 0.810. It boils at 132.0° C. It is soluble in about 50 parts of water and is miscible in all proportions with alcohol and ether. Isoamyl alcohol is the principal component of fusel oil, which also contains some isopropyl and isobutyl alcohols.

a. Physiological Response

Amyl alcohol is a poisonous substance. Some authorities attribute the bad effects of excessive consumption of alcoholic beverages to the fusel oil content. Exposure to the vapors of amyl alcohol produces a marked irritation of the eyes and respiratory tract and involuntary severe coughing. Prolonged exposure to small quantities causes headache and vertigo. The accepted maximum allowable concentration is 100 parts of amyl alcohol by volume in 1,000,000 parts of air.

[24c] L. M. Christensen and E. I. Fulmer, *Ind. Eng. Chem., Anal. Ed.*, *7*, 180 (1935).
[24d] H. H. Weber and W. Koch, *Chem.-Ztg.*, *57*, 73 (1933).

b. Detection

Isoamyl alcohol may be trapped by slowly passing the air suspected of containing it through a bubbler containing water. The alcohol may be detected by the following qualitative reaction. To 1 ml. of the collected aqueous sample, add 1 ml. of a 0.1 per cent solution of furfural and 15 ml. of concentrated sulfuric acid. Allow to stand. A pink coloration is indicative of the presence of amyl alcohol. An alternative procedure is to collect the air sample in a gas collector. Add 20 ml. of 50 per cent alcohol, restopper the collector, shake occasionally for 2–3 hours. Use 1 ml. of this solution for the test. See the Korenman method detailed below.

c. Quantitative Determination

Modified Allen-Marquardt Method.[25,26] The amyl alcohol is extracted from a saturated salt solution by carbon tetrachloride and is subsequently oxidized by means of a potassium dichromate-sulfuric acid solution. The volatile fatty acids produced are distilled and estimated by titration with 0.1 *N* alkali solution. If interfering substances such as esters and aldehydes are trapped along with the amyl alcohol, they must be removed by prior saponification and boiling under a reflux condenser with 0.5 g. of *m*-phenylenediamine hydrochloride for 1 hour. The amyl alcohol is then recovered by distillation.

Procedure. Saturate approximately the collected aqueous sample with powdered sodium chloride and add saturated sodium chloride solution until the specific gravity of the mixture is 1.10, which may be determined with a hydrometer. Extract the salt solution 4 times with purified carbon tetrachloride, using 40, 30, 20, and 10 ml. of the solvent successively. Wash the combined carbon tetrachloride solution extracts 3 times with 50-ml. portions of saturated sodium chloride solution and twice with saturated sodium sulfate solution. Transfer the carbon tetrachloride to a flask containing 50 ml. of a solution of 100 g. of potassium dichromate in 900 ml. of water and 100 ml. of sulfuric acid, and boil for 8 hours under a reflux condenser. Add 100 ml. of water and distill until only about 50 ml. remains. Add 50 ml. of water to the flask and again distill until 35 to 50 ml. is left. Use care to prevent the oxidizing mixture from caking on the side of the distilling flask. The distillate should be water white. If it is colored, discard it and repeat the determination. Titrate the distillate with 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator. One ml. of 0.1 *N* sodium hydroxide solution is equivalent to 0.0088 g. of amyl alcohol. Corks covered with tinfoil should be used in the distillation from the oxidizing mixture and preferably all-glass apparatus should be used.

Run a blank on 100 ml. of carbon tetrachloride, beginning the blank with the washing with the salt solutions.

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[25] A. H. Allen and W. Chattaway, *Analyst, 16,* 102 (1891).
[26] L. Marquardt, *Ber., 15,* 1370 (1882).

Colorimetric Method. Penniman, Smith, and Lawshe[27] developed a method for the determination of amyl alcohol which depends upon the production of unsaturated hydrocarbons with sulfuric acid and subsequent colorimetric estimation of the amyl alcohol by color reagents. Because of the extreme sensitivity of the reagents, the method can be used only on dilute solutions of amyl alcohol.

Procedure with p-Dimethylaminobenzadehyde or Salicylaldehyde Reagent. Transfer 2 ml. of the sample (diluted if necessary) with an accurate pipette to a 125-ml. Florence flask. Add 20.0 ml. of sulfuric acid, swirling the flask in a bath of cold water during the addition. Then add exactly 2 ml. of a solution of the reagent in 95 per cent alcohol, 10 mg. per ml., again swirling the flask in the cold bath.

Prepare a similar flask containing 2 ml. of a standard amyl alcohol solution, acid, and reagent.

Place the flasks simultaneously in a bath of vigorously boiling water. After 20 minutes, transfer the flasks to the cold bath. When cool add 25 ml. of sulfuric acid (1:1) and mix thoroughly by swirling. Compare the colors produced in a colorimeter of the Duboscq type or other suitable colorimeter.

Procedure with Vanillin Reagent. Proceed as directed above for the other two reagents, except for the following differences: (a) use only 10 ml. of concentrated sulfuric acid in making up the reaction mixture; (b) the vanillin solution contains 17.5 mg. of the reagent per ml. of 95 per cent alcohol.

The concentrations and times must be followed rigidly, for the reaction is not allowed to go to completion but is arbitrarily stopped after a definite length of time by chilling the reaction mixture and diluting. It is therefore necessary to run the sample and standard together.

It is best to prepare standards using, if possible, some of the isoamyl alcohol used in the industrial process. If this is impossible, isoamyl alcohol boiling at 132° C. may be used. If commercial fusel oil is the solvent employed, standards may be prepared from a mixture of isoamyl and isobutyl alcohols in the ratio 4 to 1.

Korenman Method.[28] Collect the sample in a dry flask of known volume. Add 10 ml. of ethyl alcohol and an equal volume of water. Shake for 2 to 3 hours to absorb the amyl alcohol. Transfer 1 ml. of the

[27] W. B. D. Penniman, D. C. Smith, and E. I. Lawshe, *Ind. Eng. Chem., Anal. Ed., 9,* 91 (1937).

[28] I. M. Korenman, *Arch. Hyg., 109,* 108 (1932).

aqueous alcohol mixture to a colorimeter tube, add 0.1 ml. of a 1 per cent alcoholic solution of furfural, cool, add 1.5 ml. of concentrated sulfuric acid, heat for 3 minutes in a boiling-water bath, and after cooling again compare the pink to red color produced with standards treated in the same way at the same time. The method is accurate to about ±10 per cent.

6. Cyclohexanol

Cyclohexanol is used as a stabilizer, penetrant, blending agent, and homogenizer for combinations of solvents with or without dissolved solids. It is employed in soap manufacture, in the leather, lacquer, straw-hat, textile, and artificial-silk industries. It is used in the formulation of emulsions, detergents, cutting oils, insecticides, disinfectants, shoe creams, and as a solvent for rubber, resins, and fats.

Cyclohexanol, $C_6H_{11}OH$, also known by the trade names and synonyms of hydrophenol, hexahydrophenol, Hexalin, Anol, Hydralin, and Adronol, is a water-white, slightly viscous liquid or a colorless hygroscopic crystalline solid with a camphoraceous, menthol-like odor. It boils at 161° C.; melts at 23–25° C.; has a specific gravity of 0.945 at 20/4° C.; a refractive index of 1.4602 at 20° C. It is soluble in water, 1 in 30.

Cyclohexanol is neutral, nonphenolic, and, while it will burn, is not explosive.

McConnell[29] states that it may paralyze the central nervous system and is possibly more toxic than benzene, but since it has a much lower volatility it is probably not as dangerous. The recommended maximum allowable working concentration is 100 parts per million.

Cyclohexanol may be estimated by trapping the vapor in water and then converting it to the benzoate by the addition of benzoyl chloride.[30] After refluxing and steam distilling, the residue is extracted with ether. The benzoate is recovered from the ether and identified by specific-gravity and refractive-index measurements.

Cyclohexanol and methylcyclohexanol react with catechol and concentrated sulfuric acid to give a straw color. This reaction can be used as a basis for their determination.[31]

Extract the vapor collected in a large evacuated sampling bulb (11 liters) or bottle by shaking for 5 minutes with 100 ml. of water. The water may be conveniently added by having the sampling vessel equipped with a smaller bulb containing the water connected through a stopcock with the sampling vessel itself.

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[29] W. J. McConnell, *J. Am. Med. Assoc., 109,* 762 (1937).

[30] J. Marcusson, *Chem. Ztg., 49,* 656 (1925).

[31] J. F. Treon, W. E. Crutchfield, Jr., and K. V. Kitzmiller, *J. Ind. Hyg. Toxicol., 25,* 323 (1943).

Transfer a 2-ml. aliquot to a glass-stoppered test tube (150 by 22 mm.) and add 1 ml. of freshly prepared 5 per cent aqueous catechol solution. Add 10 ml. of concentrated sulfuric acid so that it forms a layer, immediately mix thoroughly and rapidly, and then promptly place in a water bath at 100° C. After 30 minutes cool under tap water for 2–3 minutes, cool at 4–5° C. for 15 minutes, and compare with a suitable standard in a 2-inch cell of a wedge photometer at 520 or 540 mμ.

Standards should be prepared daily. The error of analysis in the range of 0.05 to 0.25 mg. of cyclohexanol and methylcyclohexanol in aqueous solution is ±0.0009 mg., corresponding to ±0.041 mg. per liter in air.

7. *Methylcyclohexanol*

Methylcyclohexanol has much the same uses as cyclohexanol, particularly in soap manufacture, in the textile and artificial-silk industry, and as a degreaser. Methylcyclohexanol, $CH_3C_6H_{10}OH$, also known by the synonyms and by trade names as hexahydrocresol, hexahydromethylphenol, methyl Hexalin, Sectol, Methlanol, Heptalin, and methyl Adronol, is an anhydrous mixture of the three isomeric *o*-, *m*-, and *p*-cyclohexanols obtained by the hydrogenation of cresols.

It is a neutral, colorless, oily liquid resembling cyclohexanol in its properties. The commercial product boils in the range 165–190° C., has a specific gravity of 0.918–0.926, and a refractive index of 1.455–1.465 at 20° C. It is soluble to about 3 per cent in water.

The fumes of this material are irritating to the nose and throat and may have some effect on the blood. The relatively high boiling point reduces the danger. The recommended maximum allowable concentration is 100 parts per million. The concentration may be estimated by the general method for solvents detailed in other sections of the text and by the method detailed above.

B. GLYCOLS, ALCOHOL-ETHERS, AND DERIVATIVES

1. *Ethylene Glycol*

The glycols have changed from the status of comparatively rare organic chemicals to that of organic chemicals which have an increasing commercial importance. The glycols are dihydroxy derivatives of the paraffins. Ethylene glycol is the simplest of these. It is now used as a solvent for waxes, resins, and dyes; for moistening tobacco; as a preservative; in the manufacture of printing pastes; in antifreeze mixtures; in explosives, dynamite; and esters, of which the most important is ethylene glycol dinitrate, used in the manufacture of low-freezing gelatin dynamites.

Ethylene glycol, $HOCH_2CH_2OH$, is a colorless, practically odorless, sweet, syrupy liquid. It is extremely hygroscopic and can absorb almost twice its weight of water. It boils at 197° C.; has a specific gravity of 1.117 at 15/15° C.; and a vapor pressure of 0.1 mm. of mercury at 20° C. It is entirely miscible with water and lowers the freezing point of the mixture, the greatest depression being obtained when the mixture consists of 60 per cent ethylene glycol and 40 per cent water by volume.

a. Toxicity and Physiological Response

Whereas Fuller[32] concluded that ethylene glycol is not toxic, more complete knowledge of its physiological response has shown that ethylene glycol and its derivatives—diethylene glycol, diethylene glycol monoethyl ether (ethyl diethylene glycol), ethylene glycol monoethyl ether (ethyl ethylene glycol), ethyl ethylene glycol acetate, 1,4-dioxane, and ethylene glycol monobutyl ether (butyl ethylene glycol)—depress the muscular and nervous tissue, have hemolytic properties, and produce more or less marked local irritation.[33] Oettingen and Jirouch determined the toxicity of the glycols by subcutaneous injection into white mice. They found that butyl ethylene glycol (ethylene glycol monobutyl ether) is by far the most toxic; ethylene glycol ranging next; diethylene glycol, the two ethyl ethers, and ethyl ethylene glycol acetate being less toxic. Further studies on the toxicity of the glycols have been made by Goldwater,[34] Greenburg,[35] and others.[36,37] The toxicology of ethylene glycol and other glycols has been discussed by Fairhall.[37a]

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[32] H. C. Fuller, *Ind. Eng. Chem.*, *16*, 624 (1924).

[33] W. F. von Oettingen and E. A. Jirouch, *J. Pharmacol.*, *42*, 355 (1931).

[34] L. Goldwater, *N. Y. State Ind. Bull.* *16*, 308, 438, 504 (1937).

[35] L. Greenburg, L. Goldwater, M. D. Mayers, W. J. Burke, and S. Moskowitz, *N. Y. State Ind. Bull.* *17*, 269 (1938).

[36] H. W. Werner, C. Z. Nawrocki, J. L. Mitchell, J. W. Miller, and W. F. von Oettingen, *J. Ind. Hyg. Toxicol.*, *25*, 374 (1943).

[37] H. W. Werner, J. L. Mitchell, J. W. Miller, and W. F. von Oettingen, *J. Ind. Hyg. Toxicol.*, *25*, 409 (1943).

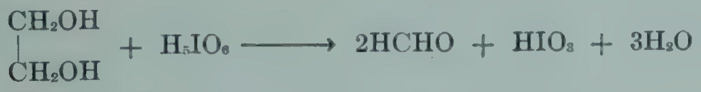
[37a] L. T. Fairhall, *Ind. Hyg. Newsletter*, *8*, No. 13 (1948).

b. Detection

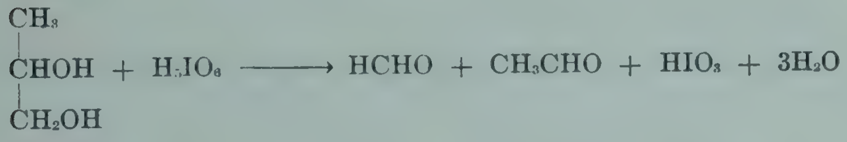
Polyhydroxy alcohols such as ethylene glycol, glycerol, and propylene glycol, which have hydroxyl groups on adjacent carbon atoms, can be broken down to formaldehyde and formic acid by treatment with excess periodic acid in the cold, the periodic acid being changed to iodic acid.[38] After the destruction of excess periodate and iodate, the formaldehyde may be detected as described in the section on methyl alcohol.

Place a small aliquot of the sample solution in a test tube. Add some 5 per cent potassium periodate solution, some N sulfuric acid solution, and allow to stand for 5 minutes. Reduce the excess periodate with a saturated solution of sulfurous acid. Add Schiff's reagent and allow to stand for half an hour. A violet to blue color is indicative of polyhydroxy alcohols.

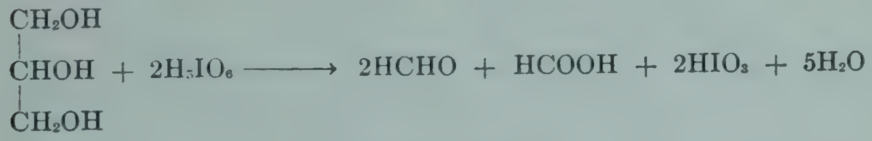
On oxidation with periodic acid, ethylene glycol yields formaldehyde, glycerol yields formic acid and formaldehyde, and propylene glycol yields formaldehyde and acetaldehyde. Diethylene glycol does not yield formaldehyde. Hence these four polyhydroxy alcohols may be differentiated:



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + H_5IO_6 \longrightarrow 2HCHO + HIO_3 + 3H_2O$$



$$\begin{array}{l} CH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + H_5IO_6 \longrightarrow HCHO + CH_3CHO + HIO_3 + 3H_2O$$



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 2H_5IO_6 \longrightarrow 2HCHO + HCOOH + 2HIO_3 + 5H_2O$$

c. Determination

The glycols may be estimated by the following variation of determining the acetyl value.[39] If the glycol has been adsorbed on a solid adsorbent, dry the adsorbent, add 1 g. of anhydrous sodium sulfate and extract with 100 ml. of acetone in a continuous extraction device for 1 hour. Distill the extract and remove the last traces of acetone by blowing air over the residue. Add 5 ml. of acetic anhydride and 2 g. of anhydrous sodium acetate and esterify the mixture by heating under a reflux condenser for 90 minutes. Neutralize to phenolphthalein with potassium hydroxide solution, hydrolyze an aliquot portion with a known volume of 0.1 *N* potassium hydroxide solution, and titrate the residual alkali with standard hydrochloric acid.

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[38] F. Feigl, *Qualitative Analysis by Spot Tests,* Elsevier, New York, 1946.

[39] O. Lazar and A. H. Meyling, *J. S. African Chem. Inst., 21,* 8 (1938); *Chem. Abstracts, 32,* 8689 (1938).

Permanganate Oxidation. Under proper conditions ethylene glycol can be oxidized completely to carbon dioxide and water by means of potassium permanganate solution.

Place 10 ml. of ethylene glycol solution of approximately 0.025 *M* concentration into a flask. Add 50 ml. of 0.01 *N* potassium permanganate solution and 30 ml. of 4 *N* sodium hydroxide solution. Allow to stand for $1^1/_2$ hours, after which period add 50 ml. of 4 *N* sulfuric acid and allow the mixture to stand for another hour. Finally, add 10 ml. of 10 per cent potassium iodide solution and titrate the liberated iodine with standard sodium thiosulfate solution. Under these conditions ethylene glycol reacts with 5 atoms of oxygen, corresponding to complete oxidation to carbon dioxide and water. A blank determination must be run on all the reagents omitting the test glycol solution.

Dichromate Oxidation. The concentration of ethylene glycol may also be determined by oxidation with potassium dichromate in concentrated sulfuric acid in the usual way.

Periodate Oxidation. By oxidation with 0.05 *N* periodic acid, 11 g. of periodic acid dissolved in water, made up to 1 liter and filtered, ethylene glycol forms formaldehyde and iodic acid. It may be estimated potentiometrically or iodometrically.[40]

Separation from Glycol-Ethers. The amount of ethylene glycol present in glycol-ether mixtures can be ascertained by use of the ditrityl ether method devised by Seikel[40a] and by the lead tetraacetate oxidation method.[40b] In the former method, the glycol is converted into its ditrityl ether which can be separated from the other monotrityl ethers and byproducts because of its relative insolubility. The ditrityl ether can then be estimated gravimetrically. In the lead tetraacetate method, the glycol is oxidized by excess lead tetraacetate in acetic acid and the decrease in the oxidizing power of the solution serves as a direct measure of the glycol content for the alkyl ethers of diethylene glycol are substantially unaffected.

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[40] N. Allen, H. Y. Charbonnier and R. M. Coleman, *Ind. Eng. Chem., Anal. Ed.*, *12*, 384 (1940).

[40a] M. K. Seikel, *Ind. Eng. Chem., Anal. Ed.*, *13*, 388 (1941).

[40b] R. C. Hockett and W. S. McClenahan, *J. Am. Chem. Soc.*, *61*, 1670 (1939).

Procedure. Heat 0.25 ml. of diethylene glycol monomethyl- or monoethyl ether in a test tube for 15 minutes on a steam bath with 1 to 2 ml. of pyridine and trityl chloride in excess over that amount calculated to convert all the ethylene glycol to its ditrityl ether and the diethylene glycol alkyl ether to its trityl ether. Leach with water, ice until the oil stiffens to a partially crystalline mass, and wash by decantation with several portions of water. Extract the gum with 20 ml. of 95 per cent alcohol. The alcohol-insoluble precipitate is the ditrityl ether of ethylene glycol and should melt at 170–180° C. If the melting point is much lower, reextract the material. Calculate the percentage of glycol from the weight of the residue.

2. Diethylene Glycol

Because of its hygroscopic and solvent properties, diethylene glycol finds much use in industry. It is used as a solvent for dyes and as a fiber softener or plasticizer in the textile industry. It is used as an anti-freeze and as a moistening agent in cigarettes and in other manufactured products. It is used in the preparation of esters and in the manufacture of synthetic resins.

Diethylene glycol, β,β'-dihydroxydiethyl ether, $HOCH_2CH_2OCH_2CH_2OH$, is a colorless, practically odorless, hygroscopic liquid with a sharply sweetish taste. It boils at 244.5° C. and at 75° C. under high-vacuum distillation between 10^{-6} or 10^{-7} mm. of mercury. It has a specific gravity of 1.118 at 20/20° C. and a refractive index of 1.4475 at 20° C. It is miscible with water, alcohol, ether, acetone, and ethylene glycol but is insoluble in benzene and carbon tetrachloride.

a. Toxicity and Physiological Response

During September and October of 1937, at least 73 persons died as a direct result of taking the drug known as "Elixir Sulfanilamide." Twenty other persons who took this elixir died, but it was not fully established that the drug was exclusively responsible. The 93 deaths occured in 15 states, as far east as Virginia and as far west as California.[41] Thus with dramatic intensity the toxicity of this compound was brought to the attention of the United States. The indiscriminate use of this solvent with the valuable drug, sulfanilamide, was responsible in some measure for the passage of the Food and Drugs Act of 1938.

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[41] U. S. Senate, 75th Congress, 2nd Session, *Document 124* (1937).

The victims of the "elixir" were ill from about 7 to 21 days. They suffered intense pain. All exhibited very much the same symptoms—stoppage of urine, severe abdominal pain, nausea, vomiting, and stupor; convulsions preceded death in some cases.

Haag and Ambrose[42] studied the physiological effect of diethylene glycol. They concluded that, in terms of milliliters per kilogram of body weight, the acute minimal fatal dose of diethylene glycol for white rats is; by intramuscular injection, 7 ml.; intravenously, 5 ml.; subcutaneously, 15 ml.; and orally, 15 ml. For rabbits the minimal fatal dose is: by intramuscular injection, 4 ml.; intravenously, 2 ml.

Rats maintained on a standard diet and receiving concentrations of diethylene glycol of 1 and 0.3 per cent in their drinking water showed slight enhancement in growth. Concentrations of 0.1 and 0.03 per cent gave growth curves practically identical with the normal controls. Likewise, the growth of rats receiving a 10 per cent solution of glycerol was as good as the controls. The ingestion of diethylene glycol in concentrations of 3 and 10 per cent proved rapidly fatal.

Geiling, Coon, and Schoeffel[41] confirmed the finding of Haag and Ambrose[42] that the ingestion of 15 ml. of diethylene glycol per kilogram in a single dose by stomach tube proves fatal to rats. They concluded, however, that this figure is no index of the toxic and possible fatal effect of the substance, if administered in small divided doses, especially since neither the fate nor the mechanism of detoxification is known. This substance possibly produces injury to certain cells at a rate faster than the repair processes take place; hence each succeeding dose may be adding to the harmful effect.

b. Detection and Determination

Diethylene glycol may be differentiated from other glycols which have hydroxyl groups on adjacent carbon atoms, in that formaldehyde is not formed with periodic acid. Diethylene glycol forms a derivative with 3,5-dinitrobenzoyl chloride. The *bis*-3,5-dinitrobenzoate of diethylene glycol recrystallized from benzene-petroleum benzine melts at 150.5 to 151.5° C.

This glycol may be estimated by methods previously detailed and by those in Chapter XII.

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[42] H. B. Haag and A. M. Ambrose, *J. Pharmacol.*, *59*, 93 (1937).

3. *Ethylene Glycol Monomethyl Ether*

Ethylene glycol monomethyl ether, more familiarly known as methyl Cellosolve, has a variety of industrial uses but the actual volume used is small in comparison with other glycol ethers. It is used as a solvent for cellulose acetate, nitrocellulose, and many natural resins and gums, and as a thinner in acetate lacquers and dopes. This compound is frequently used in the formulation of quick-drying varnishes, enamels, and wood stains. It is mentioned as an ingredient in some of the lacquer formulas of United States Government specifications. Many dyes and printing inks are aided in their action by this solvent and it is considered to be superior to glue for sealing moisture-proof transparent wrappers of certain types. It is also used in the fused-collar industry.[43]

The fused collar has gained considerable popularity because of the fact that it is nonwilting and therefore requires no starch for stiffening. The collar is made by inserting an interlining composed partly of cellulose acetate threads between the layers of cotton fabric. The entire collar is treated with a solvent which causes the cellulose acetate to jell. With the application of heat and pressure, the three layers of the collar become fused and thus produce a stiff appearance without the use of starch. This process is known as "Jaysonizing" when methyl Cellosolve is used.

Ethylene glycol monomethyl ether, $HOCH_2CH_2OCH_3$, 2-methoxymethanol, an alcohol-ether, is a volatile liquid with an agreeable odor. It boils at 124° C. and has a vapor pressure of 7 mm. of mercury at 20° C. It has a specific gravity of 0.961–0.966 at 20/20° C. and a refractive index of 1.4028 at 20° C.; its flash point is 32° C. This compound has the most rapid rate of evaporation and the lowest boiling point of the commercially available alcohol-ethers. It is miscible with water.

a. Physiological Response

Greenburg[44,45] and his co-workers contend that glycols or glycol derivatives such as the alcohol-ethers may also affect the blood or blood-forming organs, in contrast to the traditional belief that abnormal blood pictures in industry are almost always associated with (1) benzene and its derivatives, (2) certain heavy metals such as lead and arsenic, (3) radioactive substances, (4) only occasionally with halogenated hydrocarbons, and (5) rarely with such substances as hydrogen sulfide and carbon disulfide. They feel that the glycols, alcohol-ethers, and their derivatives are another group of organic chemicals that must be added to the list of hemotoxic substances. In order to avoid these toxic effects, the recommended maximum allowable concentration of ethylene glycol monomethyl ether in air for daily 8-hour exposure is 25 parts per million.[46]

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[43] L. Greenburg, M. R. Mayers, L. Goldwater, W. J. Burke, and S. Moskowitz, *N. Y. State Ind. Bull. 17*, 269 (1938); *J. Ind. Hyg. Toxicol., 20*, 134 (1938).

[44] L. Greenburg, M. R. Mayers, L. Goldwater, W. J. Burke, and S. Moskowitz, *J. Ind. Hyg. Toxicol., 20,* 134 (1938).

[45] C. E. Parsons and M. E. Parsons, *J. Ind. Hyg. Toxicol., 20,* 124 (1938).

b. Determination

Where this substance is the only volatile contaminant of an atmosphere, its concentration in that atmosphere can be determined by the general method for the determination of volatile solvents described in Chapter XII. If, however, as is much more likely, ethylene glycol monomethyl ether is only one of the components of a volatile mixture, and the general method is to be used, the approximate composition of the mixture must be known so that the concentrations may be calculated from the vapor pressures of the components of the mixture. Thus, in the fused-collar industry, one of the solvent mixtures used is composed of 67 per cent of denatured alcohol and 33 per cent of the alcohol-ether. The denatured alcohol consisted of 90 per cent alcohol, 4.4 per cent methyl alcohol, 4.7 per cent ethyl acetate, and 0.9 per cent petroleum naphtha.

If calculation is not competent to give the desired result, the alcohol-ether can be separated from the other solvents by fractional distillation. The other solvents can be estimated in the presence of one another by the usual methods and the amount of alcohol-ether can be estimated by difference.

c. Determination of Monoalkyl Ethers of Ethylene Glycol[47,48]

The methyl (methyl Cellosolve), ethyl (Cellosolve), *n*-propyl, and *n*-butyl (butyl Cellosolve) ethers of ethylene glycol can be quantitatively oxidized by potassium dichromate in concentrated sulfuric acid. Theoretically these substances should require 16, 14, 20, and 26 equivalents of oxygen, respectively, on the basis that the methyl radical is oxidized to carbon dioxide and water, the ethyl radical to acetic acid and water, and the propyl and butyl radicals to carbon dioxide, acetic acid, and water. The experiments of Werner and Mitchell indicate that the actual equivalents of oxygen consumed, using the method detailed below, were 15.7, 13.8, 19.9, and 26, respectively.

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[46] *Ind. Hyg. Newsletter, 7,* No. 8, 15 (1947).

[47] H. W. Werner and J. L. Mitchell, *Ind. Eng. Chem., Anal. Ed., 15,* 375 (1943).

[48] H. B. Elkins, E. D. Storlazzi, and J. W. Hammond, *J. Ind. Hyg. Toxicol., 24,* 229 (1942).

Procedure. Charge samplers, such as suggested in Chapter IV, of such size that the sample collected will contain not more than the glycol-ether equivalent of 50 per cent of the potassium dichromate present, with 5 ml. of 0.33 *N* potassium dichromate and 5 ml. of concentrated sulfuric acid, and evacuate. Use 6 ml. of concentrated sulfuric acid, if the *n*-propyl derivative is being estimated. Take the samples in the locale desired and re-stopper. Transfer the flasks to the laboratory and heat the stoppered flasks in a boiling water bath for the periods indicated in Table 28. Cool, transfer the contents to 500-ml. wide-mouth flasks, dilute each to approximately 300 ml., add 3 g. of potassium iodide, and titrate with 0.05 *N* sodium thiosulfate solution, using starch solution at the end of the titration as the indicator. Calculate the amount of glycol-ether found, using the factors given in Table 28.

TABLE 28

Heating Periods and Factors for Estimation of Glycol-Ethers by the Dichromate Method[47]

Ethylene glycol derivative	Reaction Mixture, per cent acid	Heating Period, minutes	Factor, 0.33 *N* $K_2Cr_2O_7$
Methyl	50	30	1.584
Ethyl	50	30	2.141
n-Propyl	50	240	1.736
n-Propyl	55	60	1.736
n-Butyl	50	120	1.514

4. Ethylene Glycol Monomethyl Ether Acetate

Ethylene glycol monomethyl ether acetate, $CH_3COOCH_2CH_2OCH_3$, methyl Cellosolve acetate, is a colorless liquid with a pleasant ester odor. It has a specific gravity of 1.0067 at 20/20° C., a boiling point of 144.5° C., and a flash point, open cup, at 140° F. This ester is completely miscible with both water and ethyl alcohol. Methyl Cellosolve acetate is used in the preparation of dopes and lacquers and is a solvent for cellulose acetate, cellulose nitrate, and various gums, oils, and resins. The recommended maximum allowable concentration for this ester is 25 parts of ethylene glycol monomethyl ether acetate per million parts of air by volume.

The concentration of this ester in air may be determined by some of the methods detailed in this chapter and in Chapter XII.

5. Ethylene Glycol Monoethyl Ether

Ethylene glycol monoethyl ether, also known as "Cellosolve," is widely used as a solvent for nitrocellulose and resins in the manufacture of lacquers and lacquer thinners. It has a particular use in making lacquers with a slight odor which are preferable for household and architectural purposes. In industry it is also used for leather finishes, varnish removers, cleaning solutions, dyeing, and textile printing.

Ethylene glycol monoethyl ether, $HOCH_2CH_2OC_2H_5$, is a colorless liquid with a mild and agreeable odor in low concentrations and a disagreeable odor in high concentrations. The pure liquid compound has a boiling point of 134.9° C., specific gravity of 0.9305 at 20/20° C., flash point at 40° C., and a vapor pressure of 4.6 mm. of mercury at 20° C. The vapors are approximately 3 times heavier than air. This alcohol-ether is completely soluble in water.

a. Physiological Response

Waite, Patty, and Yant[49] studied the physiological response of guinea pigs to ethylene glycol monoethyl ether.

> The symptoms exhibited after 18 to 24 hours' exposure to air saturated with the vapors of ethylene glycol monoethyl ether, which is a 0.6 per cent by volume mixture, were inactivity, weakness, dyspnea, and death. Exposure to 0.6 per cent by volume for 24 hours caused death at the end of the exposure; 0.3 per cent for 24 hours caused death in 24 hours following exposure; exposure to 0.6 per cent for 10 hours, 0.3 per cent and 0.1 per cent for 18 hours caused occasional death in from 1 to 8 days following exposure. Exposure to 0.6 per cent for 1 hour, 0.3 per cent for 4 hours, and 0.05 per cent for 14 hours caused no apparent harm.

It is unlikely that an atmosphere containing sufficient of the alcohol-ether to produce serious acute poisoning in 1 hour can be established at ordinary room temperatures because of the comparatively low vapor pressure of the ethylene glycol monoethyl ether.

Air saturated with alcohol-ether vapor at room temperature produces a disagreeable odor and moderate eye irritation. If these properties are heeded as warning of the occurrence of a potentially dangerous atmosphere, the aforementioned investigators believe that acute poisoning will not occur. It is well to note, however, that other investigators believe that chronic poisoning can occur with concentrations far below those of a warning nature. The recommended maximum allowable concentration for an 8-hour daily exposure is 200 parts per million.

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[49] C. P. Waite, F. A. Patty, and W. P. Yant, *U. S. Pub. Health Service, Reprint 1389* (1930).

b. Determination

In an atmosphere in which this alcohol-ether is known to be present because of the industrial processes involved, and it is the only vapor contaminant, it may be estimated by the general method for the determination of volatile contaminants in air, which is described on page 482 of Chapter XII. In those instances in which ethylene glycol monoethyl ether is a component of a solvent mixture, it may be estimated by fractional distillation of the sample. If the approximate composition of the vapor produced by the solvent is known, the amount of the alcohol-ether may be calculated from the vapor pressures.

6. Ethylene Glycol Monoethyl Ether Acetate

Ethylene glycol monoethyl ether acetate, $CH_3COOCH_2CH_2OC_2H_5$, Cellosolve acetate, is a liquid which is used as a solvent for resins and nitrocellulose. It has a specific gravity of 0.9748 at 20° C., a boiling point of 156.4° C., and a flash point of 150° F. The specific gravity of the commercial product ranges from 0.971 to 0.976 and it boils in the range of 145 to 165° C.

The recommended maximum allowable concentration is 100 parts of ethylene glycol monoethyl ether acetate per million parts of air by volume.

Its concentration in the working atmosphere can be determined by the methods detailed for solvents, in general, or by modification of the methods used for the glycol ethers.

7. Ethylene Glycol Monobutyl Ether

Ethylene glycol monobutyl ether, $HOCH_2CH_2OC_4H_9$, butyl Cellosolve, butyl ethylene glycol, is a liquid which has a specific gravity of 0.9019 at 20° C., a boiling point of 171.2° C., and a flash point of 165° F. For the commercial product, the specific gravity ranges from 0.900 to 0.905 and the boiling range is 166 to 173° C. Butyl Cellosolve is a good lacquer solvent. It is miscible with water and is also soluble in mineral oil.

The recommended maximum allowable concentration is 200 parts of butyl Cellosolve per million parts of air by volume.

It may be estimated by the methods detailed on page 482.

8. Diethylene Glycol Monoethyl Ether

Diethylene glycol monoethyl ether, more familiarly known as Carbitol, is another alcohol-ether. It is used in industry in the manufacture of safety glass, wood stains, cosmetics, the printing and dyeing of fabrics, and as a solvent for nitrocellulose, resins, and oils. It is also used for the production of esters that are used as plasticizers, for instance, Carbitol acetate and Carbitol phthalate.

Diethylene glycol monoethyl ether, $HOCH_2CH_2OCH_2CH_2OC_2H_5$, is a colorless liquid. It is slightly hygroscopic and has a mild, pleasant odor in low concentrations. It boils at 202° C., has a specific gravity of 0.990 at 20/20° C., and a refractive index of 1.4244 at 20° C. It is miscible with water and with most of the common organic solvents.

The physiological response of this compound has been discussed under ethylene glycol. It depresses the muscular and nervous tissue, has hemolytic properties, and produces local irritation. The maximum allowable concentration recommended in the State of California is 50 parts of diethylene glycol monoethyl ether per million parts of air by volume. equivalent to 0.274 mg. per liter at 25° C. and 760 mm.

This alcohol-ether may also be analyzed according to methods detailed in preceding sections and by the general methods given in Chapter XII. Its hydroxyl number factor is 0.1342.

C. ETHERS

1. Ethyl Ether

Ethyl ether, usually referred to as ether or as sulfuric ether, is used fairly extensively in industry as a solvent, diluent, denaturant, and extracting agent. It is used as a denaturant for ethyl alcohol and is often used in combination with that solvent in the manufacture of guncotton. collodion solutions, pyroxylin plastics, and rayon. It is used as an extracting agent for oils, fats, waxes, alkaloids, and acetic acid. It has many medicinal uses and, of course, is an anesthetic.

Ethyl ether, diethyl oxide, $C_2H_5OC_2H_5$, is a colorless, very mobile. very volatile, and inflammable liquid. It has a characteristic odor and a burning taste. It is hygroscopic. It boils at 34.4° C.; has a specific gravity of 0.714 at 20/20° C.; a refractive index of 1.3526 at 20° C.; and a flash point of —41° C. One part dissolves in 12.5 parts of water and it is miscible in all proportions with alcohol, petroleum ether, benzene, chloroform, etc.

Ether is a very inflammable, explosive substance. It has a tendency to form peroxides, which are themselves even more explosive. It readily forms explosive mixtures with air. It has a lower limit of explosibility of 1.8 and an upper limit of 36.5, with a range of 34.7.

a. Physiological Response

Ethyl ether is not a very poisonous substance. Its greatest hazard in industrial use is its fire hazard. Ether produces anesthesia and can cause intoxication resembling that of alcohol. During Prohibition, "bootleg" beer was "needled" with ether. It is a powerful narcotic and a concentration of 35,000 parts per million can produce unconsciousness. Where it is present in the atmosphere in sufficient quantity to produce a lethal effect, it probably kills by paralyzing the respiration. The recommended maximum allowable concentration for an 8-hour daily exposure is 400 parts of ethyl ether per million parts of air.

b. Determination

Ethyl ether may be estimated by oxidation with iodine pentoxide[50] at a temperature of 200° C. One mol of ether is equivalent to 4.8 mols of monoatomic iodine:

$$5(C_2H_5)_2O + 12\ I_2O_5 \longrightarrow 20\ CO_2 + 25\ H_2O + 24\ I$$

The air may be sampled by the vacuum-bottle method and the method for the determination of carbon monoxide by oxidation with iodine pentoxide (page 424) may be followed but the ether cannot be dried with concentrated sulfuric acid, for it is absorbed by that reagent. If carbon monoxide or acetone are present, the method cannot be applied unless corrections for both substances are made. Acetone may be removed by treatment with a saturated solution of sodium or potassium bisulfite, followed by strong potassium hydroxide solution and solid potassium hydroxide to remove sulfur dioxide formed. Either the iodine or the carbon dioxide produced by the reaction may be estimated.

Larger amounts of ether may be determined volumetrically by the diminution in volume noted by gas-burette readings before and after absorption of ethyl ether by sulfuric acid, specific gravity 1.84, with the aid of a gas pipette. The amount of ether in air may also be estimated by use of the charcoal tube adsorption gravimetric method and by use of the benzene (benzol) indicator.

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[50] H. W. Haggard, *J. Biol. Chem., 55,* 131 (1923).

2. Isopropyl Ether

The use of isopropyl ether has been greatly extended by improved methods of production, which have made possible its employment as a fuel in internal-combustion engines.[51] It is also used as a solvent.[52] Isopropyl ether, $(CH_3)_2CHOCH(CH_3)_2$, is a simple aliphatic ether which at ordinary temperatures is a colorless liquid with an odor resembling both diethyl ether and camphor. It boils at 67.5° C.; has a specific gravity of 0.7258 at 20/20° C.; a refractive index of 1.3680 at 20° C.; and a vapor pressure of 158 mm. of mercury at 20° C. The commercial product boils in the range 65–69.5° C.

The ingestion of isopropyl ether causes a rapid intense intoxication like that produced by ordinary ether. The physiological effect attributable to inhalation in the monkey, which may be assumed to resemble the effects produced in man,[51] indicates that the anesthetic and fatal concentrations of isopropyl ether in air are between 3 and 6 per cent by volume and are not widely divergent. Concentrations of 1.0 per cent or less of the vapor can be tolerated in the form of daily exposures of 1 hour or longer for 20 days without permanent damage, although evidences of intoxication may be evident. Some slight but significant blood changes are also apparent. The maximum allowable concentration is analogous to that of ethyl ether, namely, 400 parts per million.

Determination

The concentration of vapors of isopropyl ether in air may be determined by the general adsorption and combustible-indicator methods previously detailed; by the use of the interferometer and vapor-pressure methods; and by combustion in a special furnace containing a Jena "Supremax" glass tube 80 cm. in length heated to 650° C. by means of 20-gauge nichrome wire.[51] The tube is packed with cylindrical particles of copper oxide and terminates in a T connection, which enables purging or diversion of the effluent gas through an Ascarite absorber when the carbon dioxide produced by the combustion is to be collected for weighing.

Another method is a modification of the method of oxidation with standard bichromate used for ordinary ether.[53]

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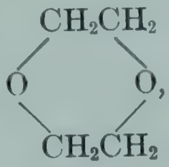
[51] W. Machle, E. W. Scott, and J. Treon, *J. Ind. Hyg. Toxicol.*, *21*, 72 (1939).

[52] H. R. Fife and E. W. Read, *Ind. Eng. Chem.*, *22*, 513 (1930).

[53] *Methods Assoc. Official Agr. Chem.* (6th ed.), 1945.

3. *Dioxane*

Dioxane is an ether of ethylene glycol. Its principal use in industry is that of a solvent. It is used in the manufacture of lacquers, celluloid, and similar products where nitrocellulose, cellulose acetate, or other cellulosic esters are used. It is to be noted, however, that dioxane does not dissolve dry nitrocellulose but does so in combination with a small amount of alcohol. It is used as a wetting agent for materials not easily wet with water, as a solvent for fats, oils, and greases; in dye baths and dye or stain compositions; in the preparation of varnishes, polishing compositions, paint and varnish removers, and detergent and cleaning preparations; in cosmetics, cements, glues, and emulsions; and as a preservative, fumigant, or deodorant.

Dioxane, 1,4-dioxane, diethylene dioxide,  is a colorless liquid of a faint, pleasant odor in very dilute concentrations.[54] It boils at 101.1° C., melts at 11° C., has a specific gravity of 1.0338 at 20° C., and a refractive index of 1.4232 at 20° C. It is miscible in all proportions with water and the common organic solvents. It forms a constant boiling mixture composed of 80 per cent dioxane and 20 per cent of water, which has a boiling point of 86.8° to 86.9° C. at 742 mm. of mercury. It has a vapor pressure of 17, 28, and 47 mm. of mercury at 10°, 20°, and 30° C. respectively.

a. Physiological Response

Dioxane produces symptoms of eye and nasal irritation, with signs of lung irritation after long exposure, and narcosis with high concentration. Concentrations of 1 per cent did not kill guinea pigs after an 8-hour exposure. Dioxane vapor possesses warning properties manifested by eye, nose, and throat irritation. Persons exposed to 0.16 per cent in air by volume immediately experienced a slight irritation of the eyes and nose, with lachrymation. Exposure to 0.55 per cent produced a marked and discomforting degree of the same symptoms with the addition of a burning sensation in the throat.

Yant[54] and co-workers concluded that health hazards from breathing the vapors of dioxane are slight under ordinary conditions of usage and reasonable exposure, but that this compound presented a hazard to life under conditions of exposure to air confined over the liquid in tanks, vats, and similar places where high concentrations might be able to accumulate.

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[54] W. P. Yant, H. H. Schrenk, F. A. Patty, and C. P. Waite, *U. S. Pub. Health Service, Reprint 1407* (1930).

These conclusions are not in accord with the observations of other investigators noted in preceding sections nor with those of Durrans,[55] Goldwater,[56] or Fairley and co-workers,[57] who point out that dioxane has insidious, long-range effects and that prolonged exposure to this substance produces damage to the kidneys and liver. Toxic amounts may be absorbed through the skin. Other symptoms are drowsiness, headache, and vertigo. The maximum allowable concentration of dioxane for daily exposures of 8 hours is 100 parts per million.

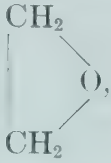
b. Determination

Dioxane reacts with tetranitromethane with the formation of a bright-yellow color.[58]

The vapors of dioxane may be sampled by trapping in water or they may be sampled and estimated directly by adsorption on weighed, air-equilibrated activated charcoal, the gain in weight, after the trapping device is air-equilibrated again, being attributed to the adsorbed dioxane. The other general methods described in Chapter XII may also be applied. Since it is inflammable, having a lower limit of explosibility of the order of benzene and gasoline, it may be estimated by the general method for the determination of combustible vapors.

4. *Ethylene Oxide*

Ethylene oxide is used as a fumigant, for its vapors are highly toxic to insects and their eggs. It is also used in combination with carbon dioxide for this purpose. Carboxide is a mixture of 1 part of ethylene oxide and 8 parts of carbon dioxide. Ethylene oxide is also used as an intermediate in the manufacture and synthesis of other organic compounds.

Ethylene oxide, 

, is a colorless gas at ordinary room temperatures. At low temperatures it is a colorless, mobile liquid, which boils

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[55] T. H. Durrans, *Solvents*, Van Nostrand, New York, 1938.
[56] L. Goldwater, *N. Y. State Ind. Bull.*, *17*, 119 (1938).
[57] A. Fairley, E. C. Linton, and A. H. Ford-Moore, *J. Hyg.*, *34*, 486 (1934).
[58] E. W. Reid and H. E. Hoffman, *Ind. Eng. Chem.*, *21*, 695 (1929).

at 10.7° C.; has a specific gravity of 0.882 at 10/10° C.; and a refractive index of 1.3597 at 7° C. It is miscible with water, alcohol, and ether in all proportions and with the other common organic solvents. It has a wide explosive range, for it has a lower limit of explosibility of 3 and an upper limit of 80 per cent by volume in air.

a. Physiological Response

Waite, Patty, and Yant[59] studied the physiological action of ethylene oxide on guinea pigs. They found that in the order of occurrence, the symptoms produced are nasal irritation, eye irritation, blood-tinged, frothy serous exudate from the nostrils, unsteadiness on feet and staggering, inability to stand, respiratory disturbances, dyspnea and gasping, and death.

> Most of these symptoms occurred with exposures to concentrations of 8.5 to 0.3 per cent by volume. Eye and nose irritation were the principal symptoms with exposure to 0.13 and 0.06 per cent; no distinct symptoms were observed with exposure to 0.025 per cent.
>
> Exposure to 5 to 10 per cent of ethylene oxide for a few minutes causes death; exposure to 0.3 to 0.6 per cent for 30 to 60 minutes is dangerous to the life of guinea pigs; 0.3 per cent is the maximum for 60 minutes without serious disturbances; and 0.025 per cent is the maximum allowable concentration for several hours without serious disturbances.

From the standpoint of relative toxicity, that is, the relative concentrations causing acute harm, ethylene oxide is less harmful than hydrogen chloride and sulfur dioxide but is more harmful than chloroform and carbon tetrachloride and is similar to ammonia.

Ethylene oxide does not possess enough odor to give distinct warning of harmful concentrations, but it does cause intolerable irritation to the eyes and nose when present in high concentrations and moderate though distinct irritation in comparatively safe concentrations. This irritation must, however, be taken as warning of a dangerous atmosphere to avoid serious injury. The recommended maximum allowable concentration for daily 8-hour exposures is 100 parts of ethylene oxide per million parts of air by volume.

b. Determination

Ethylene oxide is readily soluble in water and therefore cannot be estimated by ordinary gas-volumetric procedures. The method for detection and determination consists of passing a known volume of the suspected atmosphere through an efficient trapping device containing hydrochloric acid. The ethylene oxide reacts with the acid forming glycol chlorohydrin. The excess acid is titrated with barium hydroxide solution.

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[59] C. P. Waite, F. A. Patty, and W. P. Yant, *U. S. Pub. Health Service, Reprint 1401* (1930).

Procedure. Pass a measured volume of the air to be tested through a bubbler, such as a Milligan absorbing bottle or other efficient type of gas-scrubbing bottle, containing a known volume of standardized 2 N hydrochloric acid. Cool and transfer the sample to a titrating flask, or titrate directly in the absorbing bottle if it is an appropriate type, with standardized saturated barium hydroxide solution, using methyl orange as indicator. The quantity present can be calculated from the reaction.

$$(CH_2)_2O + HCl \longrightarrow ClCH_2CH_2OH$$

Sodium and potassium hydroxide cannot be used because they cause some hydrolysis of the glycol chlorohydrin.

An alternative procedure is to trap the ethylene oxide in 0.1 N sulfuric acid containing 50 per cent magnesium bromide and then titrating with 0.1 N sodium hydroxide solution using bromocresol green as the indicator.[60]

Ethylene oxide can also be estimated by the general method for combustible gases and by adsorption on weighed activated charcoal or silica gel. If a combustible gas indicator is employed drying agents like calcium chloride cannot be used.

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[60] O. F. Lubatti, *J. Soc. Chem. Ind., 63,* 133 (1944).

CHAPTER XVII

Acids, Esters, Aldehydes, and Ketones

The acids, esters, aldehydes, and ketones have an industrial importance of the same order as that of the alcohols, ethers, and alcohol-ethers. They are widely used as solvents, plasticizers, diluents, and even more widely used as intermediates in the manufacture of synthetics, plastics, etc., and in formulation and preparation of other materials and mixtures. Huge quantities of formaldehyde, for instance, are consumed in the manufacture of synthetic resins. Vast amounts of acetone are used for solvent purposes, especially in wartime.

Many of these substances are hazardous, some because of their toxicity and others because of the fire hazard. The toxicity of the esters ranges from the very poisonous, vesicant methyl sulfate to the almost innocuous ethyl acetate. The middle range of esters are mildly anesthetic and irritating, hence are not very dangerous to human beings under working conditions which have at least a minimum amount of protection. Massive doses of the less harmful esters, that is, concentrations in excess of 1,000 parts per million, produce depression of the central nervous system, which is manifested by lethargy, drowsiness, fatigue, loss of appetite, and general lack of energy. Some of these esters may, if exposure is continued over a long period of time, produce permanent injury.

The aldehydes rank fairly high in toxicity. They are primarily irritant but are also anesthetic. The weaker organic acids not so toxic and the ketones are possibly the least harmful of these groups but are markedly stimulating to the respiratory center.

A. ACIDS

1. *Acetic Acid*

Acetic acid is employed on a large scale industrially for the introduction of the acetyl group, as, for example, in the manufacture of cellulose acetate and cellulose acetate rayon. It is also widely used for the formation of acetate esters. It is used as an intermediate in the production of dyes and drugs, and in the artificial-leather, phenol-condensation-products, and rubber industries. It is used in textile printing, in finishing silk, and as a solvent.

Acetic acid, CH_3COOH, is a colorless liquid with a pungent odor. It boils at 118° C.; solidifies at 16.7° C.; has a specific gravity of 1.049 at 25/25° C.; and a refractive index of 1.3718 at 20° C. It is miscible with water in all proportions and also with ether and alcohol, but it is insoluble in carbon tetrachloride and carbon disulfide. It is also capable of dissolving phosphorus and sulfur. It has a lower limit of inflammability of about 4.0 per cent by volume in air.

Acetic acid has a pungent odor and in higher concentrations produces lachrymation. It penetrates the skin easily, causing dermatitis and ulcers, and inhalation of the fumes may cause irritation of the mucous membranes.[1] The recommended maximum allowable concentration is 10 parts per million parts of air.

Determination

The concentration of acetic acid vapor in air can be obtained by passing a measured volume of air through an efficient trapping device that contains a known volume of 0.02 *N* standardized alkali solution. After sampling is completed the standard alkali solution is transferred to a flask, or if the bubbler is an appropriate type, it may itself be used, and the excess of standard alkali is titrated with standard hydrochloric or sulfuric acid. The amount of acid vapor trapped is calculated from its equivalent. Each ml. of 0.02 *N* sodium hydroxide solution is equivalent to 0.0012 g. of acetic acid.

The sampling train cannot, of course, contain any link which will react with the acid vapor, such as a soda lime tube.

2. Acetic Anhydride

Acetic anhydride, $(CH_3CO)_2O$, is used along with acetic acid as an acetylating agent, especially in those instances where the water formed in the process of acetylization will interfere with production. In these instances acetic anhydride is used to react with the water that is formed to produce more acetic acid. It is used in the manufacture of artificial silk, airplane dopes, noninflammable photographic film, and as a solvent.

It is colorless liquid which boils at 139° C.; has a specific gravity of 1.080 at 15/4° C.; and a refractive index of 1.3904 at 20° C. It dissolves and reacts with water, forming acetic acid, and dissolves in alcohol, with the formation of ethyl acetate. It is soluble in chloroform and ether.

It has an odor similar to that of acetic acid, which in higher concentrations is extremely irritating, causing lachrymation. Since water hydrolyzes it slowly to acetic acid it has a physiological action similar to acetic acid. Because it is markedly irritating, however, the recommended maximum allowable concentration for an 8-hour daily exposure is 5 parts per million.

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[1] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939).

It may be estimated by trapping in 0.1 N sodium hydroxide solution with subsequent back-titration with standard acid. However, 2 mols of sodium hydroxide solution are equivalent to 1 mol of acetic anhydride.

3. Formic Acid

Formic acid is employed in the dyeing industry to replace acetic acid. It is used in the tanning industry and in the rubber industry for regenerating old rubber and for coagulating rubber latex.

Formic acid, $HCOOH$, is a colorless liquid with a pungent odor. It boils at 100.5° C.; melts at 8.4° C.; has a specific gravity of 1.220 at 20/4° C.; and a refractive index of 1.3714 at 20° C. It is inflammable and may explode when mixed with air and ignited. It is miscible with water, alcohol, ether, and glycerol. The commercial product generally contains 85–90 per cent of formic acid. It is a strong reducing agent and this property is the basis for tests for its determination.

Formic acid is irritating to the mucous membranes of the eyes, nose, and throat. A splash of it produces blisters on the skin, which tend to spread, forming new ones even after the liquid has been removed.

Determination

Formic acid may be estimated by the procedure outlined for the determination of acetic acid based on its acidity or it may be estimated by its reducing ability, as in the following method. Each ml. of 0.01 N sodium hydroxide solution is equivalent to 0.00046 g. of formic acid.

This method for the determination of formic acid is based on the reduction of potassium permanganate solution in the presence of an alkali carbonate.[2,3]

Make the solution containing the formic acid alkaline with sodium carbonate, warm, and add an excess of standard potassium permanganate solution. Acidify with sulfuric acid; add a measured volume of oxalic acid in excess of that sufficient to dissolve all of the precipitated manganese hydroxide and react with the unreduced potassium permanganate solution. Titrate the excess oxalic acid with standard potassium permanganate solution. Also titrate a volume of oxalic acid equal to that used

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[2] H. Jones, *Am. Chem. J.*, *17*, 539 (1905).

[3] F. Sutton, *Volumetric Analysis*, Blakiston, Philadelphia, 1924.

in the test as a blank. The difference between the amount of permanganate used in the blank and that used in the test determination is equivalent to the amount of potassium permanganate solution required to oxidize the formic acid.

4. Oxalic Acid

Oxalic acid is used in bleaching straw, hides, and fabrics and is an ingredient of some shoe polishes. It is also used in calico printing and dyeing and in the manufacture of dyes, intermediates, and oxalates.

Oxalic acid, $(COOH)_2.2H_2O$, is a colorless, odorless, crystalline solid. It has a specific gravity of 1.625, melts at 101° C., begins to sublime at 100° C., and sublimes freely above 125° C. It is soluble in water and alcohol. It is insoluble in benzene, chloroform, and petroleum ether.

Oxalic acid has a local caustic action on the skin and mucous membranes, and causes a bluish discoloration and brittleness of the nails. It has an irritant action on the mucous membranes of the esophagus, stomach, and intestines and in higher concentrations causes nephritis and convulsions. It causes these symptoms both as dust and as a solution formed with the moisture in the atmosphere.

Determination

Oxalic acid can be estimated by the general method detailed for acids. It can also be estimated by the well known reaction with potassium permanganate. Dilute the aqueous sample solution to about 100 ml. with carbon dioxide-free water. Add 25 ml. of 2 *N* sulfuric acid. Heat the solution to 70° C. and titrate with standard 0.1 *N* potassium permanganate solution to a faint pink persisting for at least 1 minute. One ml. of 0.1 *N* potassium permanganate solution is equivalent to 0.006302 g. of the dihydrate or 0.004501 of anhydrous oxalic acid.

Salts of oxalic acid such as sodium oxalate may be sampled by use of a fritted bubbler. The amount may then be estimated by use of the permanganate method detailed above.

B. ESTERS

Esters are the organic derivatives of acids in which the hydrogen atom of the acidic hydroxyl group has been replaced by an alkyl or aryl radical. The esters are of great importance as solvents for they are among the basic components used in some industries.

There are a large number of esters used in industry as solvents and intermediates. Some of these substances are relatively harmless, such as the ethyl and propyl acetates; others are dangerous in higher concentrations in the air, as, for example, butyl and amyl acetates; still others are very poisonous, like methyl sulfate.

Not every ester used in industry can be discussed in a limited text of this nature. The reader is referred to more special texts on solvents for this information.

Determination

The concentration of esters in air as a class may be determined by use of benzene (benzol) indicator (page 480) after special calibration of the scale.

Saponification Method. The general method for the determination of esters is based on the absorption of these esters in alcohol or water, hydrolysis of the ester by means of alkali solution, and the subsequent estimation of the excess alkali with standard acid.

$$\mathrm{RCOOR^1 + NaOH \longrightarrow RCOONa + R^1OH}$$

Sample the air to be tested by passing it through a train of bubblers containing ethyl alcohol. After sampling is complete transfer the sample to a volumetric flask and make to volume. If the ester content is low, the entire sample should be used; if it is high, an aliquot should be taken for the analysis.

Neutralize the aliquot taken for the analysis in a flask with 0.1 *N* sodium hydroxide solution, using 1 per cent alcoholic phenolphthalein solution as indicator. Add a measured amount of the standard alkali, from 25–50 ml. and boil for 10–30 minutes under a reflux condenser. If the phenolphthalein indicator color has become discharged during the refluxing, insufficient alkali has been added and another measured quantity of the standard alkali solution should be added to the test flask. After saponification is complete, cool, disconnect from the reflux apparatus, and titrate the excess alkali with 0.1 *N* hydrochloric or sulfuric acid. Calculate the number of ml. of the standard alkali solution used in the saponification of the ester, basing the calculation on the relationship of 1 ml. of the 0.1 *N* sodium hydroxide solution with the ester in question. For instance, 1 ml. of 0.1 *N* sodium hydroxide solution is equivalent to 0.0088 g. of ethyl acetate.

A variation of this method is the following.[4] Samples of the atmosphere to be tested may be taken by partly evacuated bottles, of 4 to 20 liters capacity, depending on the approximate vapor concentration, and replacing the partial vacuum with the air to be examined. The volume of the vapor-air mixture is computed from the volume of the bottle and the differential manometer readings, as detailed on page 75.

Add 10 to 50 ml. of 95 per cent alcohol to the bottle, depending on its volume; shake to facilitate absorption of the ester; and wash the solution into a flask with additional alcohol. Add a measured volume of at least 50 per cent excess standardized 0.1 N sodium hydroxide solution and reflux the reaction mixture for 30 minutes to hydrolyze the ester. Titrate the excess sodium hydroxide solution with 0.1 N sulfuric acid, using phenolphthalein as the indicator. The amount of ester present is ascertained from the volume of standard alkali used in the saponification.

1. Methyl Acetate

Methyl acetate, CH_3COOCH_3, also known as methyl acetic ether and methyl acetic ester, is a colorless liquid with a pleasant odor. It boils at 57° C. and has a specific gravity of 0.928 at 20/4° C., a refractive index of 1.3593 at 20° C., and a flash point of —16° C. Its slower limit of explosibility is 3.1 and its upper limit is 15.6. Its rate of evaporation is comparable to that of acetone. It is soluble in water and miscible with alcohol and ether.

Methyl acetate is used industrially as a substitute for acetone, as it is a solvent for nitrocellulose and for cellulose acetate. It is used as a solvent for resins and oils and in the manufacture of artificial leather.

Methyl acetate is not extremely poisonous, concentrations of the order of 10,000 parts per million causing irritation of the eyes, nose, and throat, with drowsiness and headache as subsequent symptoms, but it is readily hydrolyzed in the presence of water, yielding methyl alcohol and acetic acid, whose toxicities and physiological responses have been discussed in prior sections. This ease of hydrolysis militates against its wider industrial use. The recommended maximum allowable concentration is 200 parts per million.

It may be estimated by the general method for the determination of esters detailed above.

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[4] F. A. Patty, W. P. Yant, and H. H. Schrenk, *U. S. Pub. Health Service, Reprint 1756* (1936).

2. Ethyl Acetate

Ethyl acetate is widely used industrially as a solvent, intermediate, and ingredient of many mixtures. It is used as a solvent for nitrocellulose, lacquers, airplane dopes, varnishes, and cellulose acetate. It is used in the manufacture and formulation of artificial leather, smokeless powder, photographic film, and artificial plastics. It is employed as an intermediate in the manufacture of synthetic drugs and dyes and other organic chemicals. It is extensively used in the preparation of artificial fruit essences.

Ethyl acetate, acetic ether, $CH_3COOC_2H_5$, is a colorless liquid of pleasant, characteristic fruity odor, with a pleasant taste when diluted. It boils at 77° C. and has a specific gravity of 0.900 at 20/4° C., a refractive index of 1.370 at 25° C., and a flash point of —5° C. It is soluble in water, 1 part in 10 at 25° C., and is more soluble at lower temperatures and less soluble at higher temperatures. It is miscible in all proportions with alcohol, ether, chloroform, and acetone. It is highly inflammable, its lower limit of inflammability being 2.2 and its upper limit 11.4.

Ethyl acetate is not considered poisonous and even though it is slowly hydrolyzed by water the products that are formed are of a low order of toxicity in low concentrations. The chronic effects produced by exposure to its vapors are irritation of the mucous membranes and dermatitis, while high concentrations have a narcotic effect. It causes slight irritation of the eyes, nose, and throat at concentrations of the order of 400 parts per million. The generally accepted maximum allowable concentration for daily 8-hour exposures is 400 parts of ethyl acetate by volume per million parts of air.

3. Propyl Acetates

Propyl acetate, $CH_3COOCH_2CH_2CH_3$, is a liquid with a fruity odor. It has a specific gravity of about 0.899 and a boiling point of 101° C. One part of the ester is soluble in 60 parts of water.

Isopropyl acetate, $CH_3COOCH(CH_3)_2$, is a colorless liquid with a fruity odor. Its specific gravity is in the range of 0.87–0.90 and it boils at 88–90° C. One volume of isopropyl acetate is soluble in about 30 volumes of water.

The sensory response of isopropyl acetate was studied by Silverman, Schulte, and First.[5] They found that the eyes, nose, and throat were irritated by concentrations of the order of 200 parts per million by this solvent and that the highest concentration which the majority of subjects estimated to be satisfactory for 8-hour exposures was 100 parts per million. The maximum allowable concentration recommended for propyl acetate is 200 parts per million.

The concentration of these esters in air may be determined by some of the methods detailed in this chapter and by those in Chapter XII.

4. *Butyl Acetate*

Normal butyl acetate, $CH_3CH_2CH_2CH_2COOCH_3$, is the most widely used "medium-boiling" solvent for nitrocellulose. It is also employed in the manufacture of artificial leather, photographic film, safety glass, and plastics.

It is a colorless liquid with an agreeable ester odor in low concentrations but with a disagreeable odor in higher concentrations. It boils at 125–126° C.; has a specific gravity of 0.8826 at 20/20° C.; its refractive index is 1.3951 at 20° C.; and it has a flash point of 38° C. It is soluble in about 120 parts of water at 25° C. It is miscible with alcohol and other organic solvents. It has a lower limit of explosibility of 1.7. The commercial grade boils in the range 115.9° to 141.1° C.

The generally accepted maximum allowable concentration of *n*-butyl acetate for daily 8-hour exposures is 200 parts of the ester per million parts of air by volume, although 100 parts per million was recommended by exposed persons.[6]

a. Physiological Response

The acute physiological response of guinea pigs to air containing the vapors of a commercial grade of *n*-butyl acetate was studied by Sayers, Schrenk, and Patty.[7] Normal butyl acetate produces narcosis, terminating in death in the higher concentrations. The symptoms are principally those of eye and nasal irritation and narcosis. Animals that did not die during exposure recovered.

Commercial *n*-butyl acetate has a distinct odor and is markedly irritating to the nose and eyes of men in concentrations found to be apparently harmless to guinea pigs after a single exposure of several hours' duration. Concentrations of the vapor well below the estimated lower inflammable limit are extremely disagreeable to men from the standpoint of odor and eye and nasal irritation.

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[5] L. Silverman, H. F. Schulte, and M. W. First, *J. Ind. Hyg. Toxicol.*, 28, 262 (1946).

[6] K. W. Nelson, J. F. Ege, M. Ross, L. E. Woodman, and L. Silverman, *J. Ind. Hyg. Toxicol.*, *25*, 282 (1943).

[7] R. R. Sayers, H. H. Schrenk, and F. A. Patty, *U. S. Pub. Health Service, Reprint 1769* (1936).

At room temperature, 1.4 per cent of *n*-butyl acetate vapor in air did not kill and was not dangerous to the life of guinea pigs after exposure for 30 to 60 minutes. Exposure to concentrations of 1.0 to 1.4 per cent by volume was dangerous to the life of guinea pigs after several hours. The maximum concentration tolerated by the animals for 1 hour without serious disturbance was 0.7 per cent by volume. The maximum concentration to which the animals could be exposed for several hours with slight or no disturbances was 0.33 per cent. All of these percentages were extremely disagreeable to men exposed to them for even a short time.

b. Determination

The concentration of *n*-butyl acetate in air may be estimated by the general method described for esters. However, with commercial butyl acetate an average recovery of 92.8 per cent is obtained, therefore the determination must be corrected by the application of a factor 100/92.8, or 108.9.

5. Amyl Acetate and Isoamyl Acetate

Ordinary amyl acetate or chemically pure isoamyl acetate is one of the older and still one of the best solvents for cellulose nitrate. It is also used as a solvent for celluloid, camphor, formaldehyde synthetics, natural resins, and shellac. It is employed in the manufacture of lacquers, shoe polish, artificial silk, waterproof varnishes, bronzing liquids, and metallic paints, and in the dyeing and finishing of textiles. It is used widely in the formulation of artificial fruit flavors in combination with ethyl acetate.

Isoamyl acetate, $(CH_3)_2CHCH_2CH_2COOCH_3$, familiarly known as "banana oil" and sometimes commercially as "pear oil," is a colorless, neutral liquid with a pleasant banana-like or pear-like odor in low concentrations but with an increasingly disagreeable odor in higher concentrations. The pure liquid boils at 142° C.; has a specific gravity of 0.876 at 15/4° C.; and a refractive index of 1.400 at 21° C. The commercial grade boils in the range of 120–145° C. The technical grade of amyl acetate or fusel oil amyl acetate not only contains isoamyl acetate but also the propyl, butyl, hexyl, and other acetates. One part of amyl acetate is soluble in about 400 parts of water and is miscible with alcohol, ether, ethyl acetate, and amyl alcohol. It has a lower limit of inflammability of about 1.1.

a. Physiological Response

The familiar banana-like odor of isoamyl acetate is noticeable at very low concentrations. One part per million of air is distinctly noticeable. Because of this property it was considered for use as a warning agent for gas leaks.[8,8a]

Inhalation of even low concentrations of amyl acetate causes involuntary coughing and thus is irritating to the respiratory system. Some of the symptoms caused by inhalation of the vapors of amyl acetate are irritation of the mucous membranes of the eyes, nose, throat, and bronchial tubes. It causes headache and vertigo, fullness of the head, drowsiness, oppression in the chest, and nausea. Concentrations of 5 mg. per liter, that is, 900 parts per million, cannot be tolerated for more than 60 minutes without disturbances. The maximum allowable concentration of this compound is 200 parts per million.

Concentrations of 65,000 parts per million were insufficient to cause complete narcosis in animals[9] nor did 100,000 parts per million cause death.[10]

b. Determination

The concentrations of amyl acetate in air can be estimated by the general methods for solvent vapors or by the general method for esters detailed on page 655. One ml. of 0.1 N sodium hydroxide solution is equivalent to 0.0131 g. of amyl acetate.

Detection of Butyl and Amyl Acetates

Butyl and amyl acetates in a mixture can be detected with sulfuric acid and salicylaldehyde.[11] Dilute a portion of the mixture to be tested with 70 per cent alcohol so that 100 ml. of the resulting solution contains 0.04 ml. of the original solvent mixture. To a 5-ml. aliquot of this mixture add 25 ml. of water and a 1 per cent solution of salicylaldehyde in 70 per cent alcohol solution. Add 20 ml. of concentrated sulfuric acid. Allow to stand for 45 minutes, and add another 50 ml. of sulfuric acid. The solution develops a color resembling Tokay wine if only butyl compounds are present, whereas amyl compounds produce a deep-red

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[8] V. C. Allison and S. H. Katz, *Ind. Eng. Chem.*, *11*, 336 (1919).

[8a] S. H. Katz, V. C. Allison, and W. L. Egy, *U. S. Bur. Mines, Tech. Paper 244* (1920).

[9] K. B. Lehmann, *Arch. Hyg.*, *77*, 260 (1913).

[10] F. Koelsch, *Z. Zentralstelle Volkswohlfahrt*, *19*, 246 (1912).

[11] O. Jordan, *Technology of Solvents*, Chemical Publishing Co., New York, 1937.

coloration. This is similar to the test described for amyl alcohol (page 631).

An alternative means of identifying butyl and amyl alcohols and their esters is based on the use of cobalt thiocyanate, which dissolves in alcohol to form a blue solution.[12]

Reagent. Dissolve 12.5 g. of ammonium thiocyanate in 10 ml. of water. Add 10 ml. of this mixture to 2 ml. of a 5 per cent cobalt nitrate solution and 24 ml. of water.

Procedure. Shake 1 part of the solution to be tested with 2 parts of the reagent and allow to stand. The following colors are obtained:

	Upper Layer	Lower Layer
Isoamyl alcohol	Blue	Colorless
Isobutyl alcohol	Blue	Green-blue
On dilution with more reagent (1:6) the line of demarcation disappears and a blue solution is obtained. There is no separation on addition of water until the color changes to pink.		
n-Butyl alcohol	Blue	Colorless
Blue solution, dilution with water produces a separation. Differentiation from lower alcohols, which do not separate.		
Amyl and butyl acetate	Blue	Red
Heated almost to boiling, differentiation from amyl alcohol	Colorless	Blue

6. sec-Amyl Acetate

sec-Amyl acetate is a solvent used widely in the preparation of lacquers. It was not used commercially until about 1930, when it was made available at an industrially usuable cost. *sec*-Amyl acetate should not be confused with common or isoamyl acetate, which was discussed in a preceding section.

sec-Amyl acetate, $CH_3CH_2CH_2(CH_3)CHOCOCH_3$, is a light, clear, amber-colored liquid, which has a pleasant etheral odor in very dilute concentrations but in higher concentrations has an odor which is pungent, nauseating, and disagreeable. The commercial product boils in the range of 125–149° C.; a somewhat purer grade boils in the range of 128–134° C. The pure product has a boiling point, according to Beilstein, of 133.5° C. Its specific gravity is 0.865 at 20/15.6° C. and its refractive index is 1.4021 at 20° C. It dissolves 0.2 per cent of water at 25° C.

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[12] H. H. Weber, *Chem.-Ztg.*, *54*, 61 (1930).

a. Physiological Response

sec-Amyl acetate is somewhat less provocative of coughing than isoamyl acetate. Its physiological action was studied in some detail by Patty, Yant, and Schrenk.[13]

Commercial *sec*-amyl acetate has a distinct odor and is markedly irritating to the nose and eyes of men in concentrations found to be apparently harmless to guinea pigs after several hours' exposure. Concentrations of the vapor well below the estimated lower inflammable limit were extremely disagreeable to men from the standpoint of odor and eye and nasal irritation.

sec-Amyl acetate produces narcosis, terminating in death of guinea pigs exposed to higher concentrations. The symptoms produced on exposure were principally those of eye and nasal irritation and narcosis. They also exhibited signs of lachrymation, incoordination, and slow, nearly imperceptible respiration. Animals that did not die during exposure recovered.

At room temperature, a concentration of 0.5–1.0 per cent by volume of the vapor of secondary amyl acetate in air was not dangerous to the life of guinea pigs exposed for 30–60 minutes. Exposure to this concentration for several hours was dangerous. The maximum concentration tolerated by the animals for 1 hour without serious disturbance other than eye or nasal irritation was 0.5 per cent. The maximum concentration that produced slight or no symptoms in the animals after exposure for several hours was 0.2 per cent.

b. Determination

The concentration of the vapor of *sec*-amyl acetate in air can be estimated by use of the general method for esters (page 655). The results should, however, be multiplied by the factors 100/87, or 115, for the commercial product and 100/90, or 111, for the refined product to correct for the average recovery of 87 and 90 per cent, respectively.

7. Methyl Formate

Methyl formate, $HCOOCH_3$, is a colorless, inflammable liquid which has an agreeable, ethereal odor. It boils at 31.5° C.; has a specific gravity of 0.975 at 20/4° C.; a refractive index of 1.3440 at 20° C.; and a vapor pressure of 476.4 mm. of mercury at 20° C. About 95 per cent of the commercial product boils in the range of 31.5–32.2° C. and the ramainder between 32.2 and 33.5° C. It has a lower limit of explosibility of 5.0 and an upper limit of 22.7.

Methyl formate is used as a fumigant and larvicide for tobacco, dried fruits, and cereals. It is also used as a high-boiling refrigerant for household appliances. When used as a fumigant, its fire hazard is reduced by using it with carbon dioxide in a manner similar to ethylene oxide.

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[13] F. A. Patty, W. P. Yant, and H. H. Schrenk, *U. S. Pub. Health Service, Reprint 1756* (1936).

The recommended maximum allowable concentration for daily 8-hour exposures for this ester is 100 parts per million of air by volume.

a. Physiological Response

The physiological action of methyl formate was studied by Nuckolls[14] and in some detail by Schrenk, Yant, Chornyak, and Patty.[15] Methyl formate is an irritant and gives definite warning of its presence. Its odor is distinct in relatively safe concentrations, but owing to its pleasant nature and the occurrence of olfactory fatigue, the possibility of an explosion hazard should be recognized.

In their order of occurrence the symptoms produced in guinea pigs exposed to the vapor of methyl formate, were nose and eye irritation, lachrymation, retching movement, incoordination, narcosis accompanied by uncoordinated movements of the extremities, and death.

Exposure of the guinea pigs to a 5 per cent concentration of the vapor was lethal in 20 to 30 minutes; 1.5 to 2.5 per cent was dangerous in 30 to 60 minutes. The maximum concentration tolerated by the animals for 1 hour without serious disturbance is 0.5 per cent and the maximum concentration that was tolerated for several hours without serious disturbances was 0.15–0.20 per cent.

b. Determination

The concentration of methyl formate in air can be estimated by adsorption of the vapor on silica gel or air-equilibrated activated charcoal from a measured volume of air and determination of the gain in weight of the silica gel or activated charcoal absorption tube. Soda lime cannot, however, be used in the adsorption train, for it hydrolyzes the methyl formate. The general methods for esters are applicable for its estimation.

8. *Ethyl, Butyl and Amyl Formates*

Ethyl, butyl, and amyl formates are used in the lacquer, shoe, artificial-silk, and artificial-leather industries, and in the manufacture of safety glass.

Ethyl formate, $HCOOC_2H_5$, is a volatile liquid with an odor resembling that of acetone. It boils in the range of 53–57° C. and has a specific gravity of 0.925–0.930. It is soluble in water with some hydrolysis, and miscible with benzene. The recommended maximum allowable concentration for this ester is 100 parts per million parts of air by volume.

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[14] A. H. Nuckolls, *Nat. Bd. Fire Underwriters, Misc. Hazard, 2375* (1933).

[15] H. H. Schrenk, W. P. Yant, J. Chornyak, and F. A. Patty, *U. S. Pub. Health Service, Reprint 1773* (1936).

Butyl formate, $HCOOC_4H_9$, is a colorless liquid which boils in the range of 96–110° C. (commercial product) and has a specific gravity of 0.885.

Amyl formate, $HCOOC_5H_{11}$, is a colorless liquid with an odor resembling that of amyl acetate. The commercial product boils in the range of 110–130° C. and has a specific gravity of 0.880–0.885.

These substances have an irritant action on the mucous membranes and a paralyzing action on the central nervous system. The toxicity of the volatile formates increases with increasing molecular weight.[16]

The concentration of their vapors in air can be ascertained by the methods detailed in this section and the general methods described in Chapter XII.

9. Methacrylates

Methyl methacrylate, $CH_2{:}C(CH_3)COOCH_3$, is a liquid with a specific gravity of 0.936 at 20/4° C., a boiling point of 100–101° C., a flash point at 50° F., and a refractive index of 1.413 at 20° C. It is very slightly soluble in water and is miscible with alcohol and ether. This ester is used in the manufacture of methacrylate plastics and for organic syntheses. The commercial product contains an inhibitor.

A maximum allowable concentration of 500 parts per million, equivalent to 2.045 mg. per liter, for daily 8-hour exposures has been suggested in California.

Its concentration in air may be estimated by some of the methods detailed in this chapter and in those of Chapter XII.

Ethyl methacrylate, $CH_2{:}C(CH_3)COOC_2H_5$, is a liquid having a specific gravity of 0.910 at 25° C., a boiling point of 115–120° C., a flash point at 68° F., and a refractive index of 1.414 at 20° C. This ester is insoluble in water; it is very soluble in ether and ethyl alcohol. Ethyl methacrylate is used for the manufacture of plastics and in organic syntheses. To prevent polymerization, the commercial product contains an inhibitor.

The maximum allowable concentration of ethyl methacrylate is 400 parts of the ester per million parts of air by volume, equivalent to 1.864 mg. per liter at 25° C. and 760 mm.

Its concentration in air may be determined by the methods detailed in Chapter XII and by some of the methods described in this chapter.

[16] F. Flury and F. Zernik, *Schaedliche Gase,* Springer, Berlin, 1931.

10. Phthalates

The phthalates are used industrially as plasticizers, fixatives, and for similar uses. Diethyl phthalate is used as a camphor substitute in the manufacture of celluloid, in the formulation of lacquers, varnishes, and dopes, as a fixative for perfumes, and as a denaturant for ethyl alcohol. Dimethyl, dipropyl, dibutyl, and diamyl phthalate are all used as plasticizers.[17] They are all relatively high-boiling substances with low vapor pressures, thus dimethyl phthalate boils at 285° C. and diamyl phthalate boils at 342° C.

Ethyl phthalate, diethyl phthalate, $C_6H_4(COOC_2H_5)_2$ is a colorless, odorless, oily liquid with a bitter, disagreeable taste. It boils at 295° C.; it has a specific gravity of 1.118 and a refractive index of 1.499. It is practically insoluble in water but is miscible with alcohol, ether, and other organic solvents.

Butyl phthalate, dibutyl phthalate, $C_6H_4(COOC_4H_9)_2$, is a colorless, oily liquid which boils at 325° C., has a specific gravity of 1.05, and a refractive index of 1.490. It is slightly soluble in water but is very soluble in alcohol and ether.

The toxicity of the phthalates has not been studied to any great extent. Since they are of low volatility, the danger from inhalation of the vapors is relatively small. It is, however, well to note that the ingestion of phthalates, as experienced by the ingestion of beverages made with denatured alcohol, causes gastric disturbances.

Detection

If a relatively high concentration of phthalate ester is suspected either because of high concentration or because of long sampling, the following procedure may be used. Add 1 ml. of 10 per cent sodium hydroxide to the trapped alcoholic sample and evaporate to dryness on a steam bath. To the dry residue, add 5 ml. of concentrated sulfuric acid and warm for several minutes. Add 25 mg. of resorcinol and again heat for several minutes. Transfer the liquid to a test tube and heat to 160° C. for 5 minutes, using a paraffin bath. When cool, pour into 200 ml. of water and make alkaline. A characteristic greenish-yellow to brownish-yellow fluorescence will appear and is indicative of fluorescein derived from phthalic acid.

For small concentrations of phthalate ester proceed as follows: To the liquid sample (the absorbing solution may be either water or alcohol) placed in a porcelain dish or casserole, add 0.2 ml. of 10 per cent sodium hydroxide solution and evaporate to dryness on a steam bath. If necessary, the residue may be heated in a thermostatically controlled electric oven at 125° C. to obtain absolute dryness. To this residue add 5 ml. of concentrated sulfuric acid and warm on the steam bath for several minutes. Add not more than 25 to 40 mg. of resorcinol and again warm the mixture until solution is effected. Transfer the mixture to a test tube and heat in a paraffin bath at 160–170° C. for 10 minutes. Pour the cooled melt into 150 ml. of water and make alkaline with 10 per cent sodium hydroxide solution. If a phthalate ester was present in the air sample, the characteristic greenish-yellow fluorescence of fluorescein is at once apparent when viewed against a black background. When viewed under the ultraviolet lamp, the fluorescence is a light green.

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[17] C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, *32*, 1053 (1940).

Extreme care should be taken to have clean apparatus in running this test. A blank should be run to insure proper interpretation of the results. In all cases where a slight but decided fluorescence is obtained the solution should be allowed to stand for several days to observe any fading. Twenty-four hours should be allowed in every test to permit any pseudo fluorescence to disappear.

Approximately quantitative results may be obtained by comparison with the fluorescence produced by known quantities of a fluorescein solution.

The phthalic acid content of alkyd resins may be estimated by a method based on the inability of benzene to extract phthalic acid from acid aqueous solutions.[18]

11. Methyl Sulfate

Methyl sulfate, $(CH_3)_2SO_4$, dimethyl sulfate, is a colorless, oily liquid with a faint odor of onions. It boils with some decomposition at 188° C. and has a specific gravity of 1.335 at 15° C. and a refractive index of 1.3874 at 20° C. It is almost insoluble in water but it is slowly decomposed by it with the formation of methyl sulfuric acid and methyl alcohol, or of sulfuric acid and dimethyl ether with further decomposition to methyl alcohol and formaldehyde. It is miscible with alcohol and ether. It is a principal methylating agent and is used industrially for this purpose. Dimethyl sulfate was used as a lung irritant, lachrymator, and vesicant in World War I.

Dimethyl sulfate is not only a powerful lung irritant but it is also a lachrymator and vesicant. It affects all the mucous membranes, the conjunctiva, the respiratory system, and the skin, through which it can be absorbed into the body. Inhalation of a sufficient quantity will cause edema of the lungs. Its strong caustic action on the skin is accompanied by an analgesic action which may last for a long time after exposure. A concentration of 0.50 mg. per liter is lethal for exposures of 10 minutes or more; hence this substance is about as toxic as phosgene. Cats have been killed by exposure to 20 parts per million for 11 minutes.[19] The recommended maximum allowable concentration is 1 part of methyl sulfate per million of air.

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[18] F. W. Kerckow, *Farben-Ztg.*, *44*, 33 (1939).

Detection and Determination

Dimethyl sulfate is slowly decomposed by cold water, rapidly by warm water, and by alkalies with the formation of methyl alcohol and methyl sulfuric acid or with the production of sulfuric acid and methyl ether. These may subsequently decompose to form formaldehyde and methyl alcohol.

Boil the absorbing solution containing the suspected gas for 1 hour under a reflux condenser and distill. The presence of methyl alcohol in the distillate and of free sulfuric acid in the residue indicates dimethyl sulfate.

It may be estimated by slowly passing the air to be tested, or air through the sample being tested, through an alkali absorbing solution. Subsequently the amount of hydrolyzed sulfate present may be obtained by the barium sulfate method.

12. Tri-o-cresyl Phosphate

Tri-*o*-cresyl phosphate is used in industry as a plasticizer for pyroxylin lacquers, as a substitute for camphor in the manufacture of celluloid, and for the recovery of phenol. It is known commercially under the trade name of "Lindol."[20] The substance came into national prominence during 1930 because of an outbreak of "jake" paralysis, which was traced to ginger extract contaminated with this substance.[21,22]

Tri-*o*-cresyl phosphate, *o*-tolyl phosphate $(CH_3C_6H_4)_3PO_4$, is a colorless, odorless, oily-appearing liquid. It boils at 263–265° C. under an atmosphere of 20 mm. of mercury and has a specific gravity of 1.175 and a refractive index of 1.556. It is insoluble in water but is soluble in the usual organic solvents. It has 8 times the solvent power for phenol and 30 times the solvent power for higher tar acids than benzene has in ammoniacal liquors.

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[19] F. Flury and F. Zernik, *Schaedliche Gase*, Springer, Berlin, 1931.

[20] A. R. Smith, *N. Y. State Ind. Bull. 17*, 118 (1938).

[21] M. I. Smith, E. Elvove, P. J. Valaer, W. H. Frazier, and G. E. Mallory, *U. S. Pub. Health Repts., 45*, 1703 (1930).

[22] M. I. Smith, E. Elvove, and W. H. Frazier, *U. S. Pub. Health Repts., 45*, 2509 (1930).

a. Physiological Response

Tri-*o*-cresyl phosphate is of low volatility. A few cases of industrial poisoning have been reported as attributable to this compound, possibly because of absorption through the skin. However, it is a lethal poison if taken internally, the lethal dose being of the order of 1 g. per kilo of body weight. Two grams or less will cause a moderate degree of paralysis. Its action is persistent and cumulative. The first symptoms are gastrointestinal disturbances, followed after a symptom-free period by muscle soreness and paralysis of the extremities. Severe cases may be bedridden. It is partially excreted in the urine.

b. Detection

Place 5 ml. of the sample, trapped by one of the methods previously detailed, in a 250-ml. distillation flask. Make alkaline by the addition of 25 ml. of 0.1 N sodium hydroxide solution and collect 20 ml. of distillate. Dilute the residue in the flask and acidify by the addition of 10 ml. of N sulfuric acid. Boil and collect 20 ml. of distillate. Test for phenols in 10 ml. of the latter distillate by the methods detailed on page 699.

c. Determination

Acidify the bubbler sample with sulfuric acid. Extract with ether, wash with sodium hydroxide solution, and then evaporate the ether solution to dryness. Saponify with 25 per cent sodium hydroxide solution by heating at 100° C. for 1–2 hours. Acidify with sulfuric acid, distill, and determine the phenols. A phosphorus determination as described in Chapter IX may be made on the residue.

13. Ethyl Silicate[23]

Ethyl silicate, tetraethyl orthosilicate, $Si(OC_2H_5)_4$, is employed as a waterproofing agent for stone and concrete; as a bond in certain ceramic materials; as a solvent and vehicle in specialty surface coatings, particularly where heat resistance is required; as a vehicle for inorganic pigments to be fired on to glass; for the hardening of stone and arresting its decay and disintegration; in the manufacture of weather- and acid-proof mortars and cements; and as a source of pure silica for silica gel. All of these uses are at present rather small-scale operations.

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[23] H. F. Smyth, Jr., and J. Seaton, *J. Ind. Hyg. Toxicol.*, *22*, 288 (1940).

Ethyl silicate is a colorless liquid with a sharp though ester-like odor. It boils at 165–166° C.; has a specific gravity of 0.9356 at 20/20° C.; and is inflammable, with a flash point of 51.7° C. The commercial product boils in the range of 160–170° C. Its vapor pressure at 20° C. is 1.07 mm. of mercury; at 25° C., it is 1.47 mm.; and at 30° C., it is 2.04 mm. Because of the low vapor pressure and its flash point, it is improbable that explosive mixtures can be formed at room temperature. Ethyl silicate is slowly hydrolyzed by water to form silicic acid, yielding 28.8 per cent by weight of silica when hydrolysis is complete. It is very soluble in alcohol and completely miscible with ether.

a. Physiological Response

The chief initial injury from ethyl silicate administered intravenously is in the lungs in the form of pulmonary hemorrhages. Anemia, hematuria, secondary pneumonia, and acute nephritis are likely concomitants.[24]

> The principal symptoms exhibited by guinea pigs and rats exposed to the vapors of ethyl silicate were nasal irritation, eye irritation, lachrymation, respiratory difficulty, narcosis, and death. It was impossible to kill guinea pigs or rats in exposures of 30 minutes to concentrations of 3,070 parts of ethyl silicate per million of air. This concentration is a mist consisting of air saturated at 30° C. with excess silicate suspended as micro droplets. Saturation concentration at 25° C. is 1940 parts per million and at 30° C. is 2,680 parts per million. Exposure to a concentration of approximately 2,000 parts per million for 60 minutes is the maximum tolerated by the animals without the production of serious symptoms. The maximum concentration tolerated for exposures of several hours without causing serious disturbances is 500 parts per million[23].

Ethyl silicate has a distinct odor and is markedly irritating to the nose and eyes of man in concentrations found to be harmful to guinea pigs and rats. It has moderate warning properties in concentrations noninjurious to these animals after exposures of several hours.

The effects on human beings may be summarized briefly. A concentration of 3,000 parts per million is extremely irritating to the eyes and nose. A concentration of 1,200 parts per million stings the eyes and nose and produces involuntary lachrymation. Concentrations of the order of 700 parts per million mildly sting the eyes and nose, while a concentration of 250 parts per million makes the eyes and nose tingle slightly. The minimum concentration that can be detected by odor is 85 parts per million. A concentration of 700 parts per million is probably intolerable for more than 30 minutes.[23] The recommended maximum allowable concentration is 100 parts per million parts of air by volume.

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[24] J. A. Kasper, C. P. McCord, and W. G. Fredrick, *Ind. Med.*, 6, 660 (1937).

b. Determination

The concentration of ethyl silicate vapor in air can be determined by adsorption on air-equilibrated activated charcoal, as detailed in Chapter XII, by the general method for the determination of solvent vapors in air. Instrumental methods such as the interferometer may also be used.

C. ALDEHYDES

1. *Formaldehyde*

Formaldehyde is a gas. In industry it is often used as a water solution, known commercially as Formalin or Formol. Formaldehyde solution is used as a disinfectant and as a germicide, fungicide, and preservative. The gas is also used as a disinfectant. It is used in the manufacture of phenol-formaldehyde synthetic resins sold under trademarks such as Bakelite, Durite, Durez, Resinox, Indur, Catalin, and others. Cresol, dimethyl *o*-cresol, and *p*-tertiary amyl phenol are sometimes used in place of the phenol or in combination with it. Formaldehyde is used to make a synthetic resin with urea, commercially known under the trademarks Beetel, Plaskon, and Unite. It is also used in vinyl resins. Among other uses may be mentioned those in photography, dyeing, the rubber industry, the manufacture of artificial silk and cellulose esters, and explosives.

Formaldehyde, HCHO, methanal is a colorless gas at ordinary temperatures. It has a pungent suffocating odor which is intensely irritating to the mucous membranes. It boils at −21° C. It is very soluble in water and is soluble in alcohol and ether. It is very reactive and will combine with many substances.

The water solutions, known as Formalin or Formol, generally contain 37 per cent by weight of formaldehyde. Some water solutions contain 10–15 per cent of methyl alcohol to prevent polymerization to paraformaldehyde. This 37 per cent solution is equivalent to the 40 per cent solution which contains 40 g. of formaldehyde in 100 ml. of the solution. The specific gravity of the solution is 1.075–1.085.

a. Physiological Response

Formaldehyde has an irritating effect on the eyes, mucous membranes, and skin. It has a pungent odor, a suffocating effect, and very high concentrations are insupportable. It may cause severe coryza, conjunctivitis, and bronchitis. It combines with the proteins of the body and alters them. Formaldehyde has its main action on the upper respiratory system and is more of a protoplasmic poison[25] than a narcotic. Death may result from edema or spasm of the larynx.[26] There are numerous instances of dermatitis among workers in the manufacture of formaldehyde synthetic resins.[27]

The association of British Chemical Manufacturers[28] gave as the limit of toleration of formaldehyde a concentration of the order of 0.025 mg. per liter, or 20 parts per million. The recommended maximum allowable concentration[29-31] for exposures not exceeding 8 hours daily was 10 parts of formaldehyde by volume per million parts of air, equivalent to 0.012 mg. per liter at 25° C. At the 1948 meeting of the American Conference of Governmental Industrial Hygienists, the threshold limit adopted for formaldehyde was 5 parts of formaldehyde by volume per million parts of air.

b. Detection

The air suspected of containing formaldehyde is passed through an adequate trapping device containing water. The air should be sampled at a rate of 20 to 30 liters of air per hour and the length of time of sampling should depend upon the approximate concentration of the aldehyde in the air. When very low concentrations of formaldehyde are present in air and long sampling time is used, the formaldehyde that is trapped in water may be oxidized by the bubbling air and so be apparently lost in a determination. Schryver's method should be used where such conditions prevail.[32]

Detection With Schiff's Reagent. Prepare this reagent as described on page 614, or use the modified reagent described on page 615 in the section discussing the detection of methyl alcohol.

Procedure. Add 0.7 ml. of concentrated hydrochloric acid to 10 ml. of the sample obtained as described. Add 1 ml. of the Schiff fuchsin-sulfite or rosaniline-sulfite reagent and allow to stand. If a pink to deep-violet color develops on standing, formaldehyde is present.

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[25] Ind. Hyg. Research Lab., *U. S. Pub. Health Repts., Supplement 181* (1945).
[26] H. W. Haggard, *J. Ind. Hyg.*, *5*, 397 (1923–24).
[27] L. Schwartz, *U. S. Pub. Health Service, Bull. 229* (1936).
[28] *Assoc. Brit. Chem. Manufacturers, Quarterly Summary* (Oct.–Dec.), *5*, 58 (1934).
[29] E. C. Barnes and H. Speicher, *J. Ind. Hyg. Toxicol.*, *24*, 10 (1942).
[30] *Ind. Hyg. Newsletter*, *7*, No. 8, 15 (1947).
[31] *Am. Standards*, Z37.16-1944.
[32] R. W. Kersey, J. R. Maddocks, and T. E. Johnson, *Analyst*, *65*, 202 (1940).

Weinberger[33] Dimetol Reaction. Prepare a 5–10 per cent solution of dimethylcyclohexanedione in alcohol. This reagent is also known as dimetol and dimethylhydroresorcin. To the aqueous solution containing the aldehyde, add sodium chloride and make it faintly acid with acetic acid. Add a few drops of the reagent to the cold solution and stir vigorously. If formaldehyde or any other aldehyde is present a precipitate will form. Filter off the precipitate and recrystallize from hot water or alcohol and determine the melting point. Dimetolformaldehyde melts at 187° C.

Chromotropic Acid Reaction. To a few drops of the colorless test solution add 5 ml. of freshly prepared chromotropic acid solution, prepared by dissolving 50 mg. of chromotropic acid or its sodium salt in 100 ml. of 75 per cent sulfuric acid, and heat in a water bath for 10 minutes at 60° C. See page 616.

c. Determination

The amount of formaldehyde can be estimated quantitatively by following the procedure outlined for the determination of methyl alcohol by the Schiff reagent, page 616.

Formaldehyde may also be estimated by the Morasco[34] method for the determination of acetone (page 686). Formaldehyde acts like acetone liberating only 94.4 per cent of its acid equivalent. Each ml. of 0.1 *N* acid liberated is therefore equivalent to 0.00317 g. of formaldehyde.

Ripper's Method.[35,36] *General Method for the Estimation of Aldehydes.* This method is based on the combination of alkali busulfites with aldehydes:

$$RCHO + KHSO_3 \longrightarrow RCH(OH)SO_3K$$

The excess bisulfite is estimated iodometrically. It is to be used for larger quantities of aldehyde.

Transfer 50 ml. of a solution of potassium bisulfite containing 12 g. of potassium bisulfite, $KHSO_3$, per liter, by means of a pipette to a 150-ml. flask. Add 25 ml. of the solution to be analyzed. The test solution should not contain more than 0.5 per cent of aldehyde. Stopper the flask securely and allow to stand for 15 minutes. During this period transfer another 50 ml. aliquot of the potassium bisulfite solution to another flask and titrate with 0.1 *N* iodine solution. At the end of the 15-minute period estimate the excess of bisulfite present in the test solution with the 0.1 *N* iodine solution. The amount of aldehyde present is estimated from the difference in the two titrations, 2 mols of iodine being equivalent to 1 mol of bisulfite and therefore 1 mol of aldehyde.

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[33] W. Weinberger, *Ind. Eng. Chem., Anal. Ed., 3,* 365 (1931).

[34] M. Morasco, *Ind. Eng. Chem., 18,* 701 (1926).

[35] M. Ripper, *Monatsh., 21,* 1079 (1900).

[36] F. Sutton, *Volumetric Analysis,* Blakiston, Philadelphia, 1924.

Schryver's Method.[37,38] This method depends on the formation of an intense magenta color, when dilute solutions of formaldehyde hydrazone are treated with potassium ferricyanide solution in the presence of an excess of hydrochloric acid, the depth of color, between certain limits, being proportional to the concentration for formaldehyde present. The working range of the test is between 1 to 5 parts of formaldehyde per million of solution. Above 5 parts per million, the color produced is too intense for colorimetric estimation. As little as 0.5 part per million is detectable.

Reagent. Phenylhydrazine Hydrochloride Solution, 1 per cent.—Suspend 1 g. of phenylhydrazine in about 5 ml. of water, add 2 ml. of concentrated hydrochloric acid, specific gravity 1.16, and dilute to about 80 ml. Filter off any insoluble matter and dilute the filtrate to 100 ml.

Standard Formaldehyde Solution.—Stock Solution.—Dilute 25 ml. of 40 per cent weight/volume formaldehyde solution to 1 liter with water. One ml. of this solution is equivalent to 0.01 g. of formaldehyde. If greater accuracy is desired, the stock solution should be standardized by Ripper's method. Dilute 10 ml. of the stock solution to 1 liter with water. One ml. of this solution is equivalent to 0.0001 g. of formaldehyde. Further dilutions may be made on this basis.

Procedure. Place 10 ml. of the phenylhydrazine hydrochloride solution into a cylindrical bubbler fitted with a Jena-glass distribution tube (diameter, 0.75 in.) with fused-in fritted-glass filter disk (Type 33 c. G.1 —pore diameter 100 to 120 microns) or an equivalent device and dilute to 50 ml. with water. Aspirate through this solution, at a rate of about 10 liters per hour, such a volume of air to be tested that the final solution will contain between 1 and 5 mg. of formaldehyde per liter. The volume of air sampled should not exceed 40 liters because the reagent may become discolored.

Adjust the volume of the test solution to 50 ml. Transfer a 10-ml. aliquot to a 20-ml. Nessler tube, add 1.0 ml. of a 5 per cent, freshly prepared potassium ferricyanide solution, 4 ml. of hydrochloric acid, specific gravity 1.16, dilute to 20.0 ml. with water, mix well, and allow to stand for 10 minutes.

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[37] R. W. Kersey, J. R. Maddocks, and T. E. Johnson, *Analyst*, *65*, 203 (1940).

[38] E. C. Barnes and H. W. Speicher, *J. Ind. Hyg. Toxicol.*, *24*, 10 (1942).

Prepare simultaneously a series of standard comparison solutions in similar Nessler cylinders, using 2 ml. of the reagent phenylhydrazine hydrochloride solution; 7 ml. of water; adequate aliquots of the diluted standard solutions, for instance, 1, 2, 5 ml., etc., of a solution consisting of 10 ml. of the 0.1 mg. per ml. formaldehyde solution diluted to 1 liter; 1.0 ml. of 5 per cent. freshly prepared potassium ferricyanide solution, 4 ml. of hydrochloric acid, specific gravity 1.16; dilute to 20.0 ml. with water, mix well, and allow to stand 10 minutes. Compare the color of the test solution with those of the standard comparison solutions. Calculate the concentration from the nearest standard.

An impinger containing 1.25 per cent potassium hydroxide solution may also be used for trapping formaldehyde. It may then be estimated as detailed by the Schryver method.

N. Y. State Division of Industrial Hygiene Modification.[39] For sampling place about 35 ml. of water into two vials fitted with Aloxite stone diffusers connected in series. Use a flowmeter on the downstream side to control the rate of air flow at 30 liters per hour. Sample the air for 1 hour. If the samples are not to be analyzed within 24 hours, add sufficient aldehyde-free ethyl alcohol to make the alcohol concentration about 10 per cent by volume. Commercial absolute alcohol without further purification is generally adequate for this purpose.

Procedure. Make the sample and rinsings from the vials up to 50 ml. each with water and cool in a refrigerator before analysis. Cool the reagents employed also. Transfer a 25-ml. aliquot or smaller aliquot, if necessary, to 50-ml. Nessler tubes. Add to each tube 4 ml. of 1 per cent phenylhydrazine hydrochloride solution and 2 ml. of 5 per cent potassium ferricyanide solution. Prepare these reagents the same day they are to be used. Add to each tube 8 ml. of concentrated hydrochloric acid, mix, and make up to volume. Treat standards made up to contain 0.02 to 0.05 mg. of formaldehyde in the same manner at the same time. Place all the tubes in the refrigerator for 10 minutes, during which time a red-violet color develops if formaldehyde is present. Read in a colorimeter against the closest standard. Calculate the amount of formaldehyde in each vial from the relationship that 1.0 mg. of formaldehyde in 30 liters of air is equivalent to a concentration of 27 parts per million by volume.

Goldman-Yagoda Method.[40] Formaldehyde gas reacts rapidly with aqueous solutions of sodium bisulfite to form the nonvolatile sodium formaldehyde-bisulfite compound:

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[39] S. M. Moskowitz, J. Siegel, and W. J. Burke, *N. Y. State Ind. Bull. 19*, 33 (1940).
[40] F. H. Goldman and H. Yagoda, *Ind. Eng. Chem., Anal. Ed., 15*, 377 (1943).

$$HCHO + NaHSO_3 \longrightarrow HO.CH_2.OSO_2Na$$

This derivative is stable in slightly acid and neutral solutions. It can be decomposed only when the solution is made distinctly alkaline, hence by destroying excess bisulfite with iodine at pH 6 to 7, and subsequently liberating the sulfite combined as sulfoxylate by the proper adjustment of the hydrogen-ion concentration, the bisulfite dissociated from the formaldehyde-bisulfite complex can be estimated by direction titration with a standard iodine solution.

Reagents. Standard Iodine Solution.—Prepare 0.01 *N* iodine solution by dilution of 0.1 *N* iodine solution. The 0.01 *N* iodine solution must be standardized daily by titration against 0.05 *N* sodium thiosulfate solution.

Sodium Carbonate Buffer Solution.—Prepare a sodium carbonate buffer solution by dissolving 80 g. of sodium carbonate in about 500 ml. of water, adding 20 ml. of glacial acetic acid, and diluting to 1 liter.

Procedure. Draw air through a midget impinger containing 10 ml. of 1 per cent sodium bisulfite solution at a rate of 1 to 3 liters per minute. At the end of the sampling, transfer the bisulfite solution and the washings to a 300-ml. Erlenmeyer flask. Fill the large impinger with 100 ml. of bisulfite solution, when sampling at the rate of 28 liters per minute, and remove a 10-ml. aliquot for analysis.

Titrate the sample to a dark-blue end point with 0.1 *N* iodine solution, using 1 ml. of 1 per cent starch solution as indicator. Destroy the excess iodine by the addition of 1 to 2 drops of 0.05 *N* sodium thiosulfate solution and adjust the mixture to a faint-blue color by the dropwise addition of 0.01 *N* iodine solution.

Add 25 ml. of sodium carbonate buffer solution and titrate the liberated sulfite with 0.01 *N* iodine solution to a faint-blue end point. When the volume of solution used for the titration is less than 1 ml., it is desirable to run a blank on 10 ml. of 1 per cent sodium bisulfite solution. This blank correction does not exceed 0.10 ml. and is negligible in most estimations. One ml. of 0.01 *N* iodine is equivalent to 0.15 mg. of formaldehyde.

The method on which this reaction is based is not subject to interference by sulfur dioxide, alcohol, the halogen gases, and volatile organic acids which interfere with the determination of formaldehyde by the Schiff reagent. All aldehydes and acetone are, however, estimated.

In order to eliminate the interference of acetone, treat the test solution, after excess bisulfite has been removed, with 2 ml. of 5 per cent sodium bicarbonate solution. Remove the sulfite liberated by the bicarbonate by the addition of 0.01 *N* iodine solution, and adjust the pH by means of the sodium carbonate solution for the final titration of the formaldehyde-bisulfite complex as detailed above.

2. *Acetaldehyde*

Acetaldehyde, also called aldehyde, is important industrially because it can be manufactured from acetylene using mercuric sulfate as a catalyst. It is an intermediate in the manufacture of many synthetics, for it stands between ethyl alcohol on the one hand and acetic acid on the other. Thus it can be reduced to ethyl alcohol and oxidized to acetic acid. It is used in the manufacture of these substances and in the production of its polymer paraldehyde, phenol condensation products, synthetic rubber, dyes, and as a hardener in photography and for gelatin fibers.

Acetaldehyde, CH_3CHO, is a colorless, odorous liquid, with a characteristic pungent odor. It boils at 21° C. and has a specific gravity of 0.788 at 16/4° C. and a refractive index of 1.3316. It is miscible with water, alcohol, and ether in all proportions. It is inflammable, having a lower limit of inflammability of 4 per cent by volume in air and an upper limit of 57 per cent by volume. It polymerizes readily on treatment with sulfuric acid to form *paraldehyde*, which is a colorless liquid with a characteristic odor, boiling at 124° C., and after solidification, melting at 10.5° C. Paraldehyde is soluble in about 8 volumes of water and has a specific gravity of 0.994 at 20/20° C. Its refractive index is 1.4049 at 20° C. Paraldehyde is miscible with alcohol, chloroform, and ether. It gives off acetaldehyde on heating with dilute hydrochloric acid or on warming with a few drops of concentrated sulfuric acid.

a. Physiological Response

Acetaldehyde is irritant to the mucous membranes and in sufficient concentration will cause cyanosis. Iwanoff[41] reported that 280 parts per million had no effects on cats exposed for 7 hours to this concentration. The recommended maximum allowable concentration for an 8-hour daily exposure is 200 parts per million parts of air by volume. Because of its low limit of explosibility it is also a fire hazard.

b. Detection and Determination

Aldehyde can be detected by the formation of a mirror with the reduction of an alkaline silver nitrate solution.

[41] M. Iwanoff, *Arch. hyg.*, *73*, 32 (1911).

Alkaline Silver Nitrate Reagent.—Dissolve 3 g. of silver nitrate in a small portion of water and transfer to a 100-ml. volumetric flask. Add 3 g. of sodium hydroxide and, after the solution of the hydroxide, add 20 ml. of ammonium hydroxide solution, specific gravity 0.90. Make up to volume with water.

Procedure. Draw a measured volume of air through an adequate trapping device containing water at a rate of 20 to 30 liters per hour. After an adequate sample has been obtained, transfer the contents of the bubbler to a volumetric flask and make to volume.

Dilute 10 ml. of the sample with an equal volume of water in a glass-stoppered flask. Add 1 ml. of the alkaline silver nitrate reagent, stopper the flask, and place it in a closed closet or other dark place for 1 hour. Filter the mixture and make the filtrate acid with nitric acid. Add a few drops of hydrochloric acid. A silver chloride precipitate indicates that the alkaline silver nitrate reagent has not been reduced and, therefore, that no aldehyde is present.

c. Quantitative Determination

Aldehydes may be quantitatively estimated by the restoration of the color of fuchsin in a fuchsin-sulfite solution. The method uses alcohol and the residual aldehydes of the alcohol must be removed before the method can be applied.

Reagents. Aldehyde-free Alcohol.—Redistill 95 per cent alcohol over sodium or potassium hydroxide in the proportion of 1.5 liters of alcohol to 25 g. of the alkali. Add 2–3 g. per liter of *m*-phenylenediamine hydrochloride, digest at ordinary temperature for several days, or under a reflux condenser on a steam bath for several hours, and distill slowly, reject the first 100 ml. and the last 200 ml. of the distillate.

Fuchsin-Sulfite Solution.—Dissolve 0.05 g. of pure fuchsin in 50 ml. of water, add 0.5 g. of sulfur dioxide as a water solution, make up to 100 ml., and allow to stand until colorless. Water saturated with sulfur dioxide contains 11.3 g. of sulfur dioxide per 100 ml. at 20° C. The amount of sulfur dioxide should be estimated by titration with standard iodine solution, and the proper volume added to the fuchsin solution. This reagent solution decomposes readily, hence it should be prepared in small quantities and kept in a refrigerator.

Standard Acetaldehyde Solution.—Grind aldehyde-ammonia in a mortar with anhydrous ether and decant the ether. Repeat this operation several times and dry the purified compound in a current of air and then in vacuo over sulfuric acid. Dissolve 1.386 g. of this purified aldehyde-ammonia in 50 ml. of aldehyde-free 95 per cent alcohol, add 22.7 ml. of *N* alcoholic sulfuric acid, make up to 100 ml., and add 0.8 ml. of alcohol for the volume of the ammonium sulfate precipitate. Allow to stand overnight, and filter. This solution contains 1 g. of acetaldehyde in 100 ml. and will retain its strength. The standard for comparison is made by diluting 2 ml. of the strong aldehyde solution to 100 ml. with alcohol, 50 per cent by volume. One ml. of this diluted solution equals 0.0002 g. of acetaldehyde. This diluted solution must be made up fresh as it loses strength.

Procedure. Dilute 5–10 ml. of the aqueous sample to 50 ml. with aldehyde-free alcohol, 50 per cent by volume. Add 25 ml. of the fuchsin-sulfite solution and allow to stand for 15 minutes at 15° C. The solutions and reagents should be at 15° C. when they are mixed. Prepare standards of known strength and blanks in the same way. The nearest match is considered the concentration of the unknown. Nessler tubes or a colorimeter, if it is available, may be used.

3. *Acrolein*

Acrolein is an unsaturated aldehyde which does not find much use in industry. It is an intermediate in the manufacture of other substances. It is also used in the manufacture of artificial resins. Because of its properties it was used as a chemical-warfare agent in World War I and has been advocated as a warning agent for detecting leakage of refrigerants, such as methyl chloride, from refrigerators.[42] The principal hazard in industry attributable to acrolein is its formation where vegetable and animal oils and fats and glycerol are used at high temperatures.

Acrolein, also known as propenal and acrylic aldehyde, $CH_2{:}CHCHO$, is a colorless to yellowish liquid with a very pungent odor. It boils at 52.5° C.; its density is 0.841 at 20° C.; and it has a refractive index of 1.3998 at 20° C. and a vapor pressure of 99.4, 137.4, and 215.4 mm. of mercury at 3.3, 10, and 20° C., respectively. It is soluble in 3 parts of water and is miscible in all proportions with alcohol and ether. Chemically it has the properties of an aldehyde and of an unsaturated compound. When kept at room temperatures it polymerizes rapidly, with the formation of disacryl, which is a solid and which does not have the pungent properties of acrolein. This polymerization does not take place when acrolein is mixed with hydroquinone or benzoic acid in the proportion of 1–2 per cent of inhibitor to 98–99 per cent of acrolein. Polymerization is also inhibited by keeping the liquid acrolein at temperatures below 0.5° C.

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[42] W. P. Yant, H. H. Schrenk, F. A. Patty, and R. R. Sayers, *U. S. Bur. Mines, Rept. Invest. 3027* (1930).

a. Physiological Response and Toxicity

Acrolein is intensely irritating to the eyes and respiratory tract and because of its lachrymatory properties has been used as a chemical-warfare tear-gas agent. It not only irritates the eyes and respiratory tract but also irritates the skin and causes bronchial catarrh and conjunctivitis. Exposure to 1 part per million parts of air produces detectable eye and nose irritation in 2 to 3 minutes, moderate eye irritation with lachrymation in 4 minutes, and is painful and practically intolerable in 5 minutes. Concentrations of 5.5 parts per million of air cause painful eye and nose irritation in 20 seconds and are practically intolerable in 1 minute.

A U. S. Chemical Warfare Service study[42] states that the lowest concentration which produced 60 per cent deaths when inhaled by white mice for 10 minutes was 0.3 to 0.4 mg. per liter of air. On a volume basis this is equivalent to 133 to 178 parts of acrolein per million of air at 25° C. and 745 mm. of mercury. Sayers[43] states that 10 parts per million is lethal for most animals for exposures of a few minutes and that the maximum concentration that can be tolerated for several hours without serious symptoms is 3.3 parts per million.

The recommended maximum allowable concentration for daily exposures not exceeding 8 hours is 0.5 part per million parts of air by volume.

b. Detection

Acrolein gives the reactions of the aldehydes and consequently can be detected by the Schiff or modified Schiff reagent by the pink to violet coloration produced. It gives a color reaction with benzidine, as do the other aldehydes. If the test solution containing acrolein is added to a solution of benzidine in glacial acetic acid, an intense yellow coloration is produced. The details for the quantitative method are given below.

Treat 3–4 drops of a dilute aqueous solution of acrolein with an equal quantity of 3 per cent hydrogen peroxide solution. Allow the mixture to stand a minute, then add 5 ml. of concentrated hydrochloric acid, and 5 ml. of a 0.1 per cent solution of phloroglucinol in ether.[44] Shake the mixture for 1 minute. The hydrochloric acid layer assumes an intensely red color.[45]

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[43] R. R. Sayers, *International Critical Tables* (Vol. II), McGraw-Hill, New York, 1927.

[44] J. Pritzker, *Helv. Chim. Acta, 11,* 445 (1928); *Chem. Abstracts, 22,* 3114 (1928).

[45] W. C. Powick, *J. Agr. Research, 26,* 323 (1923); *Chem. Abstracts, 18,* 1580 (1924).

c. Determination

For the determination of relatively large quantities of acrolein, after absorption of the substance in either water or 5 per cent alcohol solution. Ripper's method may be used. The acrolein is treated with excess standard potassium bisulfite solution and the excess bisulfite is estimated by titration with standard iodine solution, as detailed on page 672.

Benzidine Method. Pass the air to be sampled through a series of bubblers containing absolute alcohol. The bubblers should be immersed in a cooling bath to minimize evaporation of the alcohol.

Transfer the contents of each bubbler to a volumetric flask. Wash the bubblers with absolute alcohol and make up to volume with the washings and additional absolute alcohol. Transfer 10 ml. of each flask to colorimeter tubes. Add 1 ml. of a 1 per cent solution of benzidine, 1 g. of benzidine acetate dissolved in 100 ml. of ice-cold acetic acid. Add 1 ml. of the reagent to each standard. Place all the tubes in a water bath, heat to boiling, discontinue the heat, and allow the tubes to remain in the bath for 15 minutes. Compare with the standards at the end of this period.

Formaldehyde, acetaldehyde, turpentine, furfural, and other substances give colors with the benzidine reagent, hence the test cannot be used without discrimination if these substances are present.

The standards are prepared by weighing a portion of absolute alcohol in a weighing bottle. A few drops of acrolein are added, the bottle is quickly restoppered, and the bottle is reweighed. This solution is transferred to a volumetric flask and is diluted with absolute alcohol so as to give a solution containing 1 mg. of acrolein per ml. This diluted solution is stable and may be used to prepare the standards. Acrolein, stabilized with hydroquinone, is commercially available. If such commercial acrolein is not available, it may be prepared from glycerol.[46]

Iodometric Estimation. Microchemical determinations of acrolein may be made by use of the iodoform reaction and by oxidation with potassium permanganate solution.[47]

Transfer a dilute aqueous solution of acrolein to a glass-stoppered bottle. Add 3 ml. of 0.01 *N* iodine solution and 1 ml. of 5 per cent potassium hydroxide solution. Acidify, after 30 minutes, with sulfuric acid. After an interval of 5 minutes, titrate the liberated iodine with 0.01 *N* sodium thiosulfate solution. At the same time run a blank determination with water. Calculate the amount of acrolein from the difference in the titrations on the basis that a gram equivalent of acrolein is 1/6 of a gram-molecular weight.

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[46] A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases*, Service to Industry, Hartford, 1936.

[47] I. M. Korenman, *J. Applied Chem. U.S.S.R.*, *8*, 1476 (1935).

Permanganate Estimation. Transfer a known volume of the test solution to a vessel and make strongly acid with sulfuric acid. Add a known volume of potassium permanganate solution. Heat for 15 minutes on a boiling-water bath. Add a known volume of standard oxalic acid in excess. Estimate the excess oxalic acid with standard permanganate solution. Run a blank determination at the same time. The amount of acrolein is estimated from the potassium permanganate used for the oxidation of the aldehyde.

D. KETONES

The ketones are used extensively as solvents. The acute response of guinea pigs to the inhalation of ketone vapors has been studied by Specht, Miller, Valaer, and Sayers.[48] Physical data and recommended maximum allowable concentrations are given in Table 29.

1. Acetone

Acetone is one of the most widely used solvents in industry. It is a solvent for fats, oils, waxes, resins, nitrocellulose, cellulose acetate, and acetylene, to mention some of the more important substances. It is used as an intermediate in the preparation of chloroform and iodoform. It is one of the ingredients of aeroplane dopes, varnishes, lacquers, explosives, celluloid, and paint and varnish removers. It is used as an extracting agent for the extraction of substances from plant and animal material. In this capacity it is used in the rubber industry and for the reclamation of used rubber. It is also employed to dewax lubricating oils. In combination with methyl alcohol it is used in the manufacture of fused collars. This process is known as "Trubenizing."

Acetone, CH_3COCH_3, is a colorless liquid that has an agreeable odor. It has a pungent, sweetish taste. It boils at 56.1° C.; it has a specific gravity of 0.7925 at 20/20° C.; a refractive index of 1.3591 at 20° C.; and a flash point of —20° C. It is miscible in all proportions with water, alcohol, chloroform, ether, and many oils. It dissolves castor oil. Acetone

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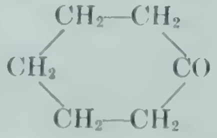
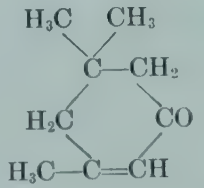
[48] H. Specht, J. W. Miller, P. J. Valaer, and R. R. Sayers, *U. S. Pub. Health Service, Nat. Inst. Health Bull. 176* (1940).

TABLE 29
Physical Data and Maximum Allowable Concentration of Ketones

Ketone	Chemical formula	Molecular weight[a]	Boiling point, deg C.[a]	Melting point, deg C.[a]	Density at 20°C.[a]	Vapor pressure[b]	Standard distillation[c]		Maximum allowable conc., ppm.[d]
							Per cent	Range, deg C.	
Acetone (dimethyl ketone)	CH_3COCH_3	58.05	56.1	−94.3	0.7915	185.0	95	56.0– 56.5	500
Ethyl methyl ketone (2-butanone)	$CH_3COCH_2CH_3$	72.06	79.6	−86.4	0.805	76.0	95	78.5– 80.0	250
Methyl propyl ketone (2-pentanone)	$CH_3COCH_2CH_2CH_3$	86.08	101.7	−77.8	0.812_{15}^{15}	30.6	85	100.0–102.0	200
n-Butyl methyl ketone (2-hexanone)	$CH_3COCH_2CH_2CH_2CH_3$	100.09	127.2	−56.9	0.830^0	10.0	80	126.0–128.0	100
Isobutyl methyl ketone (4-methyl-2-pentanone, "Hexone")	$(CH_3)_2CHCH_2COCH_3$	100.09	119.0	−84.7	0.803	15.5	80	114.0–116.0	100
Mesityl oxide (methyl isobutenyl ketone, 4-methyl-3-pentan-2-one)	$(CH_3)_2C{:}CHCOCH_3$	98.08	135	−59.0	0.863	5.8	80	128.0–132.5	50
Cyclohexanone		98.08	156.7	....	0.949	4.6	80	154.0–158.0	100

Ketone	Chemical formula	Molecular weight[a]	Boiling point, deg C.[a]	Melting point, deg C.[a]	Density at 20°C.[a]	Vapor pressure[b]	Standard distillation[c]		Maximum allowable conc., ppm.[d]
							Per cent	Range, deg. C.	
Methylcyclohexanone (mixture of 3 isomers).	$CH_3C_6H_9O$	112.09	...	....	0.917–0.921	...	..	165.0–171.0	100
n-Amyl methyl ketone (2-heptanone)........	$CH_3COCH_2CH_2CH_2CH_2CH_3$	114.11	150	....	0.822^{15}	4.2	90	150.0–152.0	
Acetonylacetone (2,5-hexanedione, diacetylethane)..............	$CH_3CO(CH_2)_2COCH_3$	114.08	194	−9	0.970	1.3	80	191.0–192.8	
n-Hexyl methyl ketone (2-octanone).........	$CH_3COCH_2CH_2CH_2CH_2CH_2CH_3$	128.12	172.7	−21.6	0.818	1.7	80	173.0–174.0	
Isophorone............		138.20	215.2	....	0.9229	0.2	..	205.0–220.0	25

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[a] *International Critical Tables*, McGraw-Hill, New York, 1927.

[b] A. K. Doolittle, *Ind. Eng. Chem.*, *2*, 1167 (1935).

[c] H. Specht, T. W. Miller, P. J. Valaer, and R. R. Sayers, *U. S. Pub. Health Service, Nat. Inst. Health Bull. 176* (1940).

[d] *Ind. Hyg. Newsletter*, *7*, No. 8, 15 (1947).

is very inflammable, for its lower limit of explosibility is 2.5 and its upper limit is 12.8; thus it has a range of explosibility of about 10 per cent by volume in air.

a. Physiological Response

While a great deal of work has been done on the toxicology of acetone, most of this work has dealt with the various phenomena associated with diabetic ketosis. Not much has been done with respect to its position as an industrial hazard. Most investigators believe that acetone is a relatively harmless substance as used industrially. Prolonged inhalation of small quantities of acetone vapors may cause irritation of mucous membranes of the eye and respiratory tract, headache, fainting, and, in much higher concentrations, narcosis. Prolonged exposure to small quantities of its vapor is irritating to the skin. A high white-blood-cell count is often associated with diabetic ketosis and some authorities believe that this is due to the chemical action of acetone.[49]

As the concentration of acetone rises and with continued exposure, there is a progressive general narcosis.[50] Acetone causes the onset of narcosis at a faster rate than methyl alcohol but is less toxic. Thus 200 mg. per liter of acetone causes narcosis in 34 minutes, whereas 200 mg. per liter of methyl alcohol causes narcosis in 94 minutes.[51,52]

Acetone in higher concentrations is more toxic for brief exposures than chloroform and is only slightly less toxic than benzene. A concentration of 20,600 parts of the vapor per million of air kills mice in 10 minutes, as compared with carbon disulfide, which requires 17,700 parts per million, benzene 19,000 parts per million, and chloroform 25,900 parts per million.[53,54] However, in low concentrations acetone is considered much less toxic than the aforementioned solvents. The recommended maximum allowable concentration[55] for daily 8-hour exposures is 500 parts of acetone by volume per million parts of air.

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[49] L. Greenburg, M. D. Mayers, L. Goldwater, and W. J. Burke, *N. Y. State Ind. Bull. 18,* 233 (1939); *J. Ind. Hyg. Toxicol., 20,* 148 (1938).

[50] H. Specht, J. W. Miller, and P. J. Valaer, *U. S. Pub. Health Repts., 54,* 944 (1933).

[51] R. M. Sklianskaya, F. I. Urieva, and L. M. Mashbitz, *J. Ind. Hyg. Toxicol., 18,* 106 (1936).

[52] L. M. Mashbitz, R. M. Sklianskaya, and F. I. Urieva, *J. Ind. Hyg. Toxicol., 18,* 117 (1936).

[53] A. C. Fieldner, S. H. Katz, and S. P. Kinney, *U. S. Bur. Mines, Tech. Paper 272* (1921).

[54] Y. Henderson and H. W. Haggard, *Noxious Gases,* Reinhold, New York, 1927.

[55] W. A. Cook, *Ind. Med., 14,* 936 (1945).

b. Detection

Iodoform Test. The presence of acetone may be detected in an atmosphere by passing the air through a bubbler containing water. The water sample may then be subjected to the iodoform test as described under the section on ethyl alcohol (page 619).

Faught Sodium Nitroprusside Test.[56] Dissolve 0.06 g. of sodium nitroprusside, $Na_2Fe(CN)_6NO.2H_2O$, in 5 ml. of water, add an equal volume of the solution to be tested, and mix well. Overlay the test solution with 5 drops of a 10 per cent ethylenediamine hydrate, $NH_2CH_2CH_2NH_2.H_2O$, solution. A pink or red zone at the interface indicates the presence of acetone. This test is sensitive to 1 part of acetone in 100,000 of solution.

A variation of the above test is performed as follows. Dissolve 0.06 g. of the nitroprusside in 5 ml. of water. Add an equal volume of the sample solution and mix well. Make slightly acid with acetic acid. Overlay with ammonium hydroxide solution. The appearance of a violet color at the interface is indicative of the presence of acetone.

c. Quantitative Determination

Messinger's Method.[57,58] Acetone reacts with iodine in the presence of alkali to form iodoform and acetic acid. This is the principle of the following method.

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3H_2O + 3NaI$$

The acetone sample may be obtained by trapping it in *N* sodium hydroxide solution in a bubbler, and the alkaline solution from the sampling may be used for the method. If water was used as the absorbent, then the sample must be added to sodium hydroxide solution.

Transfer 25 ml. of *N* sodium hydroxide solution to a 250-ml. glass-stoppered bottle, add 25 ml. of the aqueous sample or conversely add 25 ml. of the *N* sodium hydroxide solution used for sampling to a 250-ml. glass-stoppered flask, add 25 ml. of water, and then add 35 ml. of 0.1 *N* iodine solution.[59] Shake constantly during the addition of the iodine solution and allow to stand for 15 minutes. Add 26 ml. of *N* hydrochloric acid solution and titrate the excess iodine with 0.1 *N* sodium thiosulfate solution, using 1 ml. of 1 per cent starch solution as indicator. Run a blank determination on the same quantity of reagents, and deduct the number of ml. of 0.1 N iodine solution used in the blank from that consumed in the determination. Each ml. of 0.1 N iodine solution is equivalent to 0.0009675 g. of acetone. The presence of alcohol does not interfere.

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[56] H. J. Schaeffer, *Am. J. Pharm., 98,* 643 (1926).

[57] J. Messinger, *J. Soc. Chem. Ind., 18,* 138 (1889).

[58] L. F. Goodwin, *J. Am. Chem. Soc., 42,* 39 (1920).

[59] G. L. Stahly, O. L. Osburn, and C. H. Werkman, *Analyst, 59,* 319 (1934).

A variation of this method is the following.[60] Place 25 ml. of 0.1 N iodine solution and 5 ml. of 20 per cent sodium hydroxide in an appropriate absorption device. Draw through a measured volume of air. After sampling is finished, acidify the sample solution with 2 N hydrochloric acid solution and titrate the excess iodine with 0.1 N sodium thiosulfate solution using starch as the indicator.

Morasco Method.[61] In this method, acetone is trapped by drawing the air through bubblers containing 0.2 per cent hydroxylamine hydrochloride solution. The amount of acetone is estimated by titrating the hydrochloric acid liberated through the formation of the ketoxime, with standard sodium hydroxide solution.

The reaction is expressed by the equation

$$(CH_3)_2CO + NH_2OH.HCl \longrightarrow (CH_3)_2CONOH + HCl + H_2O$$

The liberated acid can be titrated in the presence of methyl orange.

Reagent. Hydroxylamine Hydrochloride, 0.2 per cent Solution—Dissolve about 12 g. of hydroxylamine hydrochloride crystals, $NH_2OH.HCl$, in about 800 ml. of water. Add methyl orange indicator and titrate carefully with 0.1 N sodium hydroxide to a neutral point. Dilute to 6,000 ml. and add sufficient methyl orange to give the solution a golden-yellow color. The solution keeps for about 2–3 days but gradually becomes slightly acid and must be neutralized again before use or else a fresh quantity must be prepared.

Procedure. Aspirate the atmosphere to be sampled through two absorbers having a column of at least 40 ml. high of hydroxylamine hydrochloride reagent solution at a rate not exceeding 20 to 25 liters per hour. If an aspirator bottle is used, the volume sampled may be assumed to equal the volume of liquid let out of the aspirator. Combine the solutions in the absorbers and titrate with 0.1 N sodium hydroxide solution until the test mixture is nearly neutral. Wait about 20 seconds. More acid will be liberated. Titrate again. Each time less acid is liberated. After about the third or fourth trial, approach the end point very closely and compare with a control containing acetone to aid in determining the end point with the aid of light reflected from a white background. Stir the mixture occasionally for 1 minute. When the solution liberates no appreciable amount of acid in 1 minute, the reaction is finished. Each ml. of 0.1 *N* sodium hydroxide solution is equivalent to approximately 0.00614 g. of acetone. The analyst should determine this equivalent by standardizing each fresh purchase of hydroxylamine hydrochloride against known amounts of pure acetone.

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[60] Elliott and J. Dalton, *Analyst, 44,* 132 (1919).

[61] M. Morasco, *Ind. Eng. Chem., 18,* 701 (1926).

2. *Ethyl Methyl Ketone (2-Butanone)*

Ethyl methyl ketone, also known as Butanone and methyl ethyl ketone, $CH_3COCH_2CH_3$, is used as a solvent in the artificial-leather and lacquer industries, in the manufacture of smokeless powder, and in colorless synthetic resins. It is also used in paint removers. It is a colorless liquid with an odor resembling that of acetone. It boils at 79.6° C., has a specific gravity of 0.805 at 20/4° C., and has a refractive index of 1.3814 at 15° C. The commercial product boils in the range 78.5–90.7° C.

a. Physiological Response

The acute response of guinea pigs to the vapors of ethyl methyl ketone was studied by Patty, Schrenk, and Yant.

Butanone has a distinct odor and is markedly irritating to the nose and eyes of man in concentrations found to be harmful to guinea pigs. It has moderate warning properties producing irritation of the eyes and nose, in concentrations apparently harmless to guinea pigs after several hours exposure. Flammable mixtures of the vapor in air are practically intolerable to man because of the odor and of the eye and nose irritation.

> The symptoms exhibited by guinea pigs upon exposure were principally those of eye and nose irritation, and narcosis, the latter being apparently the most significant. Animals that did not die during exposure recovered.[62]
>
> At room temperature, 10 per cent butanone vapor in air did not kill guinea pigs in a few minutes. Exposure to 5–10 per cent butanone vapor was dangerous to the life of guinea pigs after 30 to 60 minutes. One per cent was the maximum amount for 60 minutes exposure without serious disturbance and 0.3 per cent of the vapor in air was the maximum amount that was tolerated for several hours without serious disturbances.

Investigations[63] have shown that human beings are irritated by 350 parts per million, hence the recommended maximum allowable concentration is 250 parts of 2-butanone per million parts of air by volume.[63a]

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[62] F. A. Patty, H. H. Schrenk, and W. P. Yant, *U. S. Pub. Health Service, Reprint 1702* (1935).

[63] K. W. Nelson, J. F. Ege, M. Ross, L. E. Woodman, and L. Silverman, *J. Ind. Hyg. Toxicol., 25,* 282 (1943).

b. Determination

The concentration of butanone vapor in air can be determined by the general method for the adsorption of vapors on air-equilibrated charcoal or silica gel.

A chemical method devised by Patty, Schrenk, and Yant[62] is the following. Pipette 50 ml. of *N* sodium hydroxide solution into a flask, which is closed by a rubber stopper fitted with a glass stopcock. Connect the flask in series with a mercury U-gauge and partially evacuate it; then close the stopcock. Fill the flask by vacuum displacement. Calculate the volume of air-vapor sample taken from the U-gauge measurement at the end of the evacuation procedure and at the prevailing temperature and barometric pressure. Shake the flask to absorb the ketone and add an excess of 0.1 *N* iodine solution slowly. Allow to stand for 15 minutes, then neutralize with 2 *N* sulfuric acid and add a slight excess of 0.3–0.5 ml. Determine the excess iodine by titration with 0.05 *N* sodium thiosulfate solution.

This method is a variation of the Messinger method detailed on page 685. The average recovery of butanone of the aforementioned investigators was 107 per cent. Cassar[64] has shown that if the reaction is the following:

$$CH_3CH_2COCH_3 + 3I_2 + 3NaOH \longrightarrow CHI_3 + CH_3CH_2COOH + 3NaI + 2H_2O$$

in which 6 mols of iodine per mol of ketone is taken as 100 per cent recovery, a recovery of 110.6 per cent is actually obtained. This increase is apparently due to the influence of a secondary reaction in which 10 mols of iodine react with 1 mol of ketone:

$$CH_3CH_2COCH_3 + 5I_2 + 4NaOH \longrightarrow 2CHI_3 + CH_3COOH + 4NaI + 3H_2O$$

The values obtained for the amount of butanone vapor in air must be multiplied by a factor to account for the secondary reaction, namely by 100/107, or 0.935.

3. Methyl Propyl Ketone (2-Pentanone)

Methyl propyl ketone, ethylacetone, known commercially as Pentanone, $CH_3CH_2CH_2COCH_3$, is a colorless liquid having an odor resembling that of acetone with a somewhat more ethereal character. It is an organic solvent and is used as such for nitrocellulose and Vinilite products. It may also be used in the production of lacquers and varnish and lacquer removers.

[63a] Threshold limit value adopted April, 1948, meeting American Conference of Governmental Industrial Hygienists.

[64] H. A. Cassar, *Ind. Eng. Chem.*, *19*, 1061 (1927).

It boils at 102° C., has a specific gravity of 0.809 at 20/4° C., and a refractive index of 1.3895 at 20° C. The commercial product boils from 98.5 to 109° C. It is almost insoluble in water but is miscible in all proportions with alcohol and ether. The approximate inflammable limits are 1.5 and 8 per cent by volume in air.

a. Physiological Response

The physiological action of methyl propyl ketone on guinea pigs was studied by Yant, Patty, and Schrenk.[65]

Pentanone has a strong odor and is markedly irritating to the nose and eyes of human beings in concentrations found to be harmful to guinea pigs. It also has a distinct odor and moderate to marked irritation to human beings in concentrations producing but slight to no sign of response in guinea pigs after several hours. The inflammable range of mixtures with air is extremely disagreeable to human beings because of odor and eye and nasal irritation.

> Pentanone produces narcosis in guinea pigs, terminating in death in higher concentrations. Symptoms are principally eye and nasal irritation, followed by narcosis. Animals that do not die during exposure recover.
>
> At room temperature, 5 per cent of pentanone vapor in air did not kill guinea pigs in a few minutes. Exposures to concentrations of 3.0–5.0 per cent by volume were dangerous to the life of guinea pigs after 30–60 minutes. Exposures to concentrations of 0.8–1.0 per cent were dangerous to the life of the animals after several hours. The maximum concentration tolerated by the animals for 1 hour without serious disturbance was 0.5 per cent and this concentration was found to be very irritating to men even for short exposure. The maximum amount to which the animals could be exposed for several hours without serious disturbance was 0.2–0.4 per cent. The maximum concentration that produced no or slight symptoms in the animals after several hours was 0.15 per cent. This concentration was found by men to have a strong odor and moderate to marked irritation of the eyes and nasal passages, although no definite reaction was noted in the guinea pigs even after $13^1/_2$ hours exposure.

The recommended maximum allowable concentration for this ketone is 200 parts per million parts of air by volume.

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[65] W. P. Yant, F. A. Patty, and H. H. Schrenk, *U. S. Pub. Health Service, Reprint 1739* (1936).

b. Determination

The amount of methyl propyl ketone vapor in air may be estimated by the method described for ethyl methyl ketone. The correction factor attributable to the secondary reaction is 100/106, or 0.943.

4. Butyl Methyl Ketone (2-Hexanone)

Butyl methyl ketone, also known as hexanone and methyl butyl ketone and incorrectly as methyl butanone, is a colorless liquid. It boils at 127° C. A commercial grade of the substance has a specific gravity of 0.8132 at 20/15.6° C., boils within the range 120.1 to 137.2° C., and represents about 86.8 per cent ketone as determined by acetylation. The approximate inflammable limits are 1.2 and 8 per cent by volume in air. Hexanone is an organic solvent and is used as such for nitrocellulose and Vinilite products. It is also used in the manufacture of lacquers and in varnish and lacquer removers.

a. Physiological Response

Commercial hexanone in a concentration of 0.1 per cent has a distinct odor and is moderately irritating to the nose and eyes of human beings though apparently harmless to guinea pigs after several hours exposure. The inflammable range is extremely disagreeable to human beings from the standpoint of odor and eye and nasal irritation.

The principal symptoms produced in guinea pigs exposed to the vapors of butyl methyl ketone were nasal irritation, eye irritation, lachrymation, incoordination, narcosis, dyspnea, gasping, and death. Animals that did not die during exposure recovered.[66]

At room temperature, 2 per cent of hexanone vapor by volume in air did not kill guinea pigs after exposure for a few minutes. Exposures to concentrations of 1.0–2.0 per cent by volume were dangerous to the life of guinea pigs in 30–60 minutes. Exposures to concentrations of 0.4–0.6 per cent were dangerous to life after several hours. The maximum concentration tolerated by the animals for 1 hour without serious disturbance was 0.3 per cent. This concentration was found to be very irritating to human beings even for short exposures. The maximum concentration to which animals could be exposed for several hours without serious disturbances was 0.15 per cent. The maximum concentration that produced slight or no disturbances was 0.1 per cent. This concentration was found by human beings to have a strong odor and moderate eye and nasal irritation, although no definite reaction was noted in guinea pigs even after 13$^1/_2$ hours exposure.

The recommended maximum allowable concentration for daily 8-hour exposures is 100 parts of butyl methyl ketone per million parts of air by volume.

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[66] H. H. Schrenk, W. P. Yant, and F. A. Patty, *U. S. Pub. Health Service, Reprint 1747* (1936).

b. Determination

The concentration of butyl methyl ketone in air may be estimated by the methods described for ethyl methyl ketone, given on page 688. The correction factor attributable to incomplete yield is 100/97, or 103. Analytical results must be multiplied by this factor to give a corrected result.

5. *Isobutyl Methyl Ketone*

Isobutyl methyl ketone is used industrially in making lacquers and varnishes. It has been suggested as a diluent and as a denaturant for ethyl alcohol.

Isobutyl methyl ketone, methyl isobutyl ketone, known commercially as Hexone, and synonymous with 4-methyl-2-pentanone, CH_3COCH_2-$CH(CH_3)_2$, is a colorless liquid. It boils at 119° C. and has a density of 0.803 and a refractive index of 1.3949 at 20° C. The commercial product boils in the range of 112–118° C. and has a vapor pressure of 25 mm. of mercury at 20° C.

The inhalation of vapors of isobutyl methyl ketone causes irritation of conjunctival and nasal mucosa in man at concentrations below 0.1 per cent by volume, although this concentration is well tolerated by guinea pigs. This indicates good warning properties.

At higher concentrations marked irritation is exhibited by guinea pigs, as evidenced by lachrymation and salivation. A progressive narcosis occurs, causing lowering of body temperature, respiratory rate, and heart rate. A loss of static control, consciousness, and the deeper reflexes follows. Death finally ensues at 1.0 per cent concentration in about 4 hours and in progressively shorter periods at higher concentrations. Complete recovery can be effected by removal of the animals at any but the terminal stages.[67]

The recommended maximum allowable concentration is 100 parts of isobutyl methyl ketone per million parts of air by volume.

Determination

The concentration of the vapor of isobutyl methyl ketone in air can be estimated by the following variation of Messinger's method[68] (page 685).

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[67] H. Specht, *U. S. Pub. Health Repts.*, *53*, 292 (1938).

[68] W. H. Reinhart, as quoted by H. Specht, *U. S. Pub. Health Repts.*, *53*, 292 (1938).

Fit a 1-liter calibrated Florence flask with a one-hole rubber stopper having a tube equipped with a stopcock. Transfer 50 ml. of 1 *N* sodium hydroxide solution to the flask, connect to a vacuum pump and manometer, and evacuate. Flush a sampling line with the atmosphere to be tested.

Record the reading on the mercury gauge, close the stopcock, and connect the flask to the sampling line. Allow the flask to fill with the atmosphere to be tested at barometric pressure. Calculate the volume of air-vapor sample from the reading of the mercury gauge and the observed barometric pressure, correcting for the 50 ml. occupied by the sodium hydroxide solution and the air contained in the upper section of the stopcock.

After collecting the sample, shake the flask to absorb the vapor in the sodium hydroxide solution. In order to avoid any loss of vapor, cool the flask to reduce the inside pressure, and draw in an excess of 0.1 *N* iodine solution through the stopcock. Rinse the stopcock several times with water. Shake the flask vigorously and allow to stand for 30 minutes at room temperature to allow the reaction to go to completion. Open the stopcock carefully to relieve the pressure. Rinse the stopcock, stopper, and flask with water and add 25 ml. of 2 *N* sulfuric acid. Titrate the excess iodine immediately with 0.1 *N* sodium thiosulfate solution, using 1 per cent starch solution as indicator.

The average recovery for this ketone by this method because of factors attributable to secondary reactions, which were discussed previously, is 104 per cent, hence results must be multiplied by a factor of 100/104, or 0.962.

6. *Mesityl Oxide*

Mesityl oxide, $(CH_3)_2C{:}CHCOCH_3$, 4-methyl-3-penten-2-one, isopropylideneacetone, methyl isobutenyl ketone, is a colorless, oily liquid boiling at 128.7° C., with a specific gravity of 0.9569 at 20° C. and a refractive index of 1.446 at 16° C. Mesityl oxide will dissolve 3.4 per cent of its weight of water and conversely water will dissolve 2.8 per cent of its weight of this ketone. Mesityl oxide is miscible with alcohol and ether. This ketone is a good solvent for nitrocellulose, ethylcellulose, low-viscosity cellulose acetate, and vinyl copolymer resins.

The response of guinea pigs and rats to repeated inhalation of the vapors of mesityl oxide has been studied.[69] No effect was found after the concentration was reduced to 50 parts per million of this ketone with thirty 8-hour exposures. Single exposures indicated that this ketone has greater acute and narcotic action than isophorone. The recommended maximum allowable concentration is 50 parts of mesityl oxide per million parts of air.

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[69] H. F. Smyth, Jr., J. Seaton, and L. Fischer, *J. Ind. Hyg. Toxicol.*, 24, 46 (1942).

Smyth and his co-workers measured higher concentrations of mesityl oxide in air by means of an interferometer. Concentrations too dilute for this instrument were estimated by means of adsorption on activated carbon.

7. *Cyclohexanone*

Cyclohexanone is used in the textile, lacquer, and leather industries. It is a solvent for cellulose esters and ethers, dyes, resins, shellac, bitumen, oils and fats, etc. It is used for metal degreasing, in paint removers, and in printing inks.

Cyclohexanone, $C_6H_{10}O$, pimelic ketone, also known by the trade names of Hexanone, Sextone, and Anon, is a colorless liquid with an odor suggestive of peppermint and acetone. It boils at 156.7° C. and has a refractive index of 1.4526 at 15.3° C. and a flash point of 54° C. The commercial product boils in the range of 152–157° C. and has a specific gravity of 0.944–0.9456. It is nonexplosive and does not attack metals. At 10° C., 100 ml. of water will dissolve about 15 g., but its solubility decreases with increase in temperature, so that at 30° C. only about 5 g. will dissolve. It is miscible with most organic solvents.

The physiological response of animals to cyclohexanone has been studied by Treon, Crutchfield, and Kitzmiller.[70] They concluded that the maximum safe concentration of the vapor of this solvent is below 190 parts per million (0.75 mg. per liter). Nelson and his co-workers[71] found that workers were irritated at 75 parts per million. The recommended maximum allowable concentration is 100 parts per million.

The concentrations of cyclohexanone vapor in air can be estimated by the hydroxylamine method (page 686).

$$C_5H_{10}CO + NH_2OH.HCl \longrightarrow C_5H_{10}C{=}NOH + HCl + H_2O$$

Collect the sample as described above using a 1-liter Florence flask but charge the flask with 100 ml. of a 0.2 per cent solution of hydroxylamine hydrochloride and evacuate. Titrate the liberated hydrochloric acid using 0.05 *N* sodium hydroxide solution and methyl orange-xylene cyanole[72] as indicator. One ml. of 0.1 *N* sodium hydroxide is equivalent to 0.0098 g. of cyclohexanone.

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[70] G. F. Treon, W. E. Crutchfield, Jr., and K. V. Kitzmiller, *J. Ind. Hyg. Toxicol.*, *25*, 323 (1943).

[71] K. W. Nelson, J. F. Ege, Jr., M. Ross, L. E. Woodman, and L. Silverman, *J. Ind. Hyg. Toxicol.*, *25*, 282 (1943).

Cyclohexanone and methylcyclohexanone may also be estimated by their reaction with *m*-dinitrobenzene, yielding a pink color.

Obtain grab samples with the device described for cyclohexanol (page 632) and extract the hexanones with absolute alcohol. Transfer a 10-ml. aliquot to a 25-ml. volumetric flask and add 1 ml. of a 1 per cent solution of *m*-dinitrobenzene in absolute alcohol. Add 10 ml. of water and warm at 60° C. for 15 minutes. Add 2 ml. of 0.3 *N* aqueous potassium hydroxide solution and warm again at 60° C. for 10 minutes. Refrigerate at 4–5° C. for 12–18 hours, and make to volume with 50 per cent ethyl alcohol. Compare with freshly prepared standards in a 2-inch cell of a wedge photometer at 540 mμ. The error of analysis in the range of 0.50 to 1.88 mg. for cyclohexanone in 50 per cent aqueous alcohol is ±0.026 mg. corresponding to ±0.024 mg. per liter in air.

8. *Methylcyclohexanone*

Methylcylohexanone, $CH_3C_6H_9O$, Methylanon, is a mixture of three isomeric ketones. It is a colorless liquid with a specific gravity of 0.917–0.921 at 20° C., a boiling range of 165–171° C., and an index of refraction of 1.442. It is employed industrially for purposes similar to those mentioned for cyclohexanone.

Treon and co-workers[70] found that the maximum safe concentration for the prolonged exposure of rabbits to this solvent was in the range of 182 to 514 parts per million, equivalent to 0.82–2.31 mg. per liter. The recommended maximum allowable concentration is 100 parts of methylcyclohexanone per million parts of air.

Methods for the estimation of this ketone in air have been detailed under its homologue, cyclohexanone. In the *m*-dinitrobenzene method, the maximum error of analysis of methylcyclohexanone in the range of 1.0 to 5.0 mg. in 50 per cent aqueous alcohol is ±0.069 mg., corresponding to ±0.063 mg. per liter in air.

9. *Isophorone*

Isophorone is a good solvent for nitrocellulose and for Vinylite resins. Isophorone:

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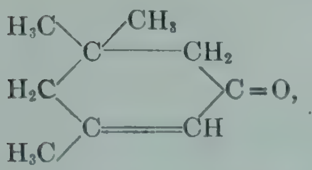
[72] K. C. D. Hickman and R. P. Linstead, *J. Chem. Soc.*, *121*, 2502 (1922).



3,5,5-trimethyl-2-cyclohexen-1-one, is a high-boiling ketone, boiling at 215° C. It has a specific gravity of 0.9229 at 20° C. and a flash point of 205° C. The commercial product has a specific gravity in the range of 0.920 to 0.925 at 20° C. and a boiling range of 205–220° C. Water will dissolve 1.2 per cent of its weight of isophorone and conversely isophorone will dissolve 4.3 per cent of its own weight of water.

The response of guinea pigs and rats to repeated inhalation of vapors of isophorone has been studied.[73] These studies indicated that this ketone is one of the most toxic ketones. The recommended maximum allowable concentration for this ketone is 25 parts of isophorone per million parts of air by volume.

Smyth and his co-workers used an interferometer to measure higher concentrations of isophorone in air in their studies. Concentrations too dilute for measurement with an interferometer were estimated by means of adsorption on activated carbon.

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[73] H. F. Smyth, Jr., J. Seaton, and L. Fischer, *J. Ind. Hyg. Toxicol.. 24,* 46 (1942).

CHAPTER XVIII

Phenolic Compounds; Aniline and Other Organic Nitrogen Compounds

A. PHENOLIC COMPOUNDS

1. Phenol

Phenol is used industrially in the manufacture of phenol-formaldehyde resins, which are sold under various trade names such as Bakelite, Durite, Durez, Resinox, Indur, Catalin, etc. In some of these, cresol, dimethyl *o*-cresol, and *p*-tertiary amyl phenol may be used instead of or in combination with the phenol. It is also used in the manufacture of many organic compounds to be used for medicinal, industrial, and textile purposes. It is widely used as a disinfectant and germicide.

Phenol, C_6H_5OH, commonly termed carbolic acid, is a colorless, crystalline solid with a very characteristic odor. When it is anhydrous and free from cresols it melts at 43° C.; boils at 182° C.; has a specific gravity of 1.071; has a refractive index of 1.5425 at 41° C.; and a flash point of 79° C. It is soluble in water, about 1 g. in 15 ml. of water, and is very soluble in alcohol, ethyl ether, chloroform, glycerol, and many other organic solvents. It is, however, insoluble in petroleum ether.

a. Toxicity and Physiological Response

Phenol is a well-known poison and has often been used with criminal intent and as a means of suicide. Deaths have been reported from its use in industry. It causes about 20 per cent of the dermatitis cases in the phenol-formaldehyde industry.[1,2] Some of the symptoms exhibited by exposure to phenol are erosion of the skin, eczema, irritation of the respiratory organs, digestive disturbances, symptoms of degeneration of the blood, emaciation, nephritis, gangrene, and jaundice.

Phenol is not only a skin irritant but is a local anesthetic as well, so that burns from it may not be felt until serious damage has been done. It can be absorbed from the skin and appear in the urine, where it imparts a smoky color.

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[1] L. Schwartz, *U. S. Pub. Health Service, Bull. 229* (1936).

[2] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939).

A maximum allowable concentration of 5 parts per million equivalent to 0.019 mg. per liter has been recommended in California.

b. Detection

Phenol vapor in air may be sampled by passing the air through a bubbler containing water or a sodium hydroxide solution. If trapped in water, the phenol may be preserved for subsequent analysis by the addition of a little sodium hydroxide solution with the formation of sodium phenolate.

The addition of a few drops of Millon's reagent to 1 ml. of the aqueous sample and heating produces a red color in the presence of phenol, salicylic acid, and cresols. To prepare Millon's reagent, dissolve 1 part of mercury in 1 part of fuming nitric acid. Dilute this solution with twice its volume of water. Decant the clear solution after waiting 24 hours.

Another well-known test for phenol is the ferric chloric reaction. Add drop by drop to a 5 ml. aliquot of the test solution a dilute solution of ferric chloride. In the presence of phenol and other phenols like salicylic acid a violet color is produced.

Extremely sensitive tests for the presence of phenol are those made with the Gibbs' reagent, 2,6-dibromoquinonechloroimide, and diazotized sulfanilic acid. These tests will be described in detail below.

c. Determination

Bromine Method.[3] This method is designed for larger amounts of phenols. Take an aliquot of the air sample, collected by passing the air through a fritted bubbler containing *N* sodium hydroxide solution, estimated to contain about 10 to 20 mg. of phenol or cresols in terms of phenol, and transfer to a 500-ml. glass-stoppered flask. Approximately neutralize and add sufficient water to make the volume just 200 ml. Add, by means of an accurate pipette, 25 ml. of potassium bromide solution, containing 250 g. of KBr dissolved in water and made to 1 liter. Add 10 ml. of hydrochloric acid (1:1) and place in a water bath at 25° C. Let stand until the temperature of the solution is 25° C. Add by means of an accurate pipette exactly 25 ml. of potassium bromate solution containing 3 g. of $KBrO_3$ dissolved in water and made to 1 liter. Mix well, then let stand at 25° C. and keep at that temperature, within 1° C., for exactly 60 minutes, shaking two or three times during this period. At the end of this time, add 25 ml. of potassium iodide solution consisting of 200 g. KI dissolved in water and made to 1 liter.

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[3] R. D. Scott, *Ind. Eng. Chem., Anal. Ed.,* 3, 67 (1931).

Mix well, and let stand at 25° C. for exactly 30 minutes, shaking two or three times during this period.

Titrate the liberated iodine with 0.1 N sodium thiosulfate solution and add 1 per cent starch solution near the end of the titration, disregarding any return of the blue starch-iodine color. Run a blank determination on the reagents in the same manner.

The difference between the two titrations multiplied by 0.0015675 equals the weight of phenol and cresols in terms of phenol. This weight divided by the volume of air sampled will give the weight of phenol per unit volume.

This method is based on formation of tribromophenol by the bromination of phenol with the bromine solution produced by the use of potassium bromide-potassium bromate mixture.[4,5]

Colorimetric Determination. Gibbs' Method.[6,7] Phenol in low concentrations of the order of 5 to 100 parts per billion of solution (5 to 100 micrograms of phenol per liter of solution) may be estimated colorimetrically by means of the reaction with 2, 6-dibromoquinonechloroimide and with diazotized sulfanilic acid. With 2, 6-dibromoquinonechloroimide, phenol reacts to form an indophenol. It couples with diazotized sulfanilic acid to form highly colored azophenol dyes.

Reagents. Alkaline Sodium Borate Solution.—Dissolve 15 g. of anhydrous sodium tetraborate, $Na_2B_4O_7$, in 900 ml. of warm water. Add 3.27 g. of sodium hydroxide in the form of a 20–40 per cent solution and make up to 1 liter. Five ml. of this solution added to 100 ml. of water should yield a solution with a pH of 9.6.

Dibromoquinonechloroimide Solution.—Either an aqueous or an alcoholic solution may be used. To prepare the aqueous solution, grind 0.04 g. of 2, 6-dibromoquinonechloroimide in a mortar with 10 ml. of water until the intermediate is broken up very finely. Wash into a brown glass-stoppered bottle and dilute to approximately 100 ml. Shake for 10 minutes and filter through filter paper. This solution decomposes very rapidly and should not be used after 20 minutes.

To prepare the alcoholic solution of the intermediate, dissolve 0.1 g. of 2, 6-dibromoquinonechloroimide in 25 ml. of 95 per cent ethyl alcohol and place in a small brown glass-stoppered bottle. This solution will keep for 3 or 4 days if placed in a cool, dark place. For the determination,

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[4] W. F. Koppeschaar, *Z. anal. Chem.*, *15*, 233 (1876).

[5] L. V. Redman, A. J. Weith, and F. P. Brock, *Ind. Eng. Chem.*, *5*, 389 (1913).

[6] H. D. Gibbs, *J. Biol. Chem.*, *72*, 649 (1927).

[7] *Standard Methods of Water Analysis, Am. Pub. Health Assoc.* (8th ed.), 1936.

dilute 5 ml. of this solution to 100 ml. with water in a brown bottle. This solution must be used immediately as it is decomposed rapidly by sunlight.

Stock Phenol Solution.—Dissolve 1 g. of reagent phenol in water and make up to 1 liter. One ml. of this solution contains 1 milligram of phenol. Standardize this solution by means of the bromide-bromate method detailed above.

Phenol Solution for Comparison Standards.—Dilute 1 ml. of the stock phenol solution to 1 liter with phenol and chlorine-free water. Chlorine-free water may be prepared by boiling distilled water in the open so that 25 per cent of its volume is volatilized. The remainder of the water is mixed with 10–25 parts per million of activated charcoal and filtered through three No. 40 Whatman filter papers in a Büchner funnel with the aid of suction.

Procedure. Collect the sample by passing the air through N sodium hydroxide solution in a fritted bubbler. Dilute the aqueous sample so that it contains from 5–100 parts of phenol per billion of solution (5 to 100 micrograms of phenol per liter of solution.) Make approximately neutral. Prepare phenol standards containing 0, 5, 10, 20, 30, 40, 50, 60, 80, and 100 parts of phenol per billion of solution by transferring 0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, and 10.0 ml. aliquots of the phenol solution for comparison standards to Nessler tubes and diluting to 100 ml. with phenol and chlorine-free water. Transfer aliquots of the sample to Nessler tubes and dilute to 100 ml. Add to each sample and standard 5 ml. of alkaline sodium tetraborate solution to yield a solution having a pH of 9.6 ± 0.3 pH. Add to each standard and sample 1.5 ml. of the alcoholic solution of 2, 6-dibromoquinonechloroimide or 2 ml. of the aqueous solution of the Gibbs' reagent. Allow at least 4 hours to pass before making color comparisons and preferably allow to stand overnight.

If preferred the color comparisons can be made by extracting the blue color formed by the interaction of phenol and the imide with solvents.[8] Among those that may be used are isobutyl alcohol, *n*-butyl alcohol, amyl alcohol, and ethyl acetate. In the alcohols the color will remain blue, in the ethyl acetate it will change to red.

p-Dimethylphenylenediamine Method. A variation of this reaction is the use of p-nitrosodimethylaniline,[9] which must be reduced to the diamine by zinc dust prior to use, or else *p*-dimethylphenylenediamine may be used directly.[8]

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[8] Morris B. Jacobs, *Chemical Analysis of Foods and Food Products,* Van Nostrand, New York, 1946.

[9] G. U. Houghton and R. G. Pelly, *Analyst, 62,* 117 (1937).

The following directions may be used for a qualitative test. To an aliquot of the sample, add 4 drops of 5 per cent sodium bicarbonate solution (5 g. of sodium bicarbonate, $NaHCO_3$, dissolved in water and made up to 100 ml.), 4 drops of 0.1 per cent diamine reagent (0.1 g. *p*-dimethylphenylenediamine dissolved in 100 ml. of water), and then sodium hypochlorite solution containing 0.05 per cent of available chlorine until the pink color first produced changes to colorless or blue. The sodium hypochlorite solution may be prepared by dissolving 60 g. of sodium carbonate and 40 g. of bleaching powder in 400 ml. of water, filtering, and diluting the filtrate so that it contains 0.05 per cent of available chlorine. Allow the reaction mixture to stand for a few minutes for the color to develop and then shake out the dye formed with either chloroform or carbon tetrachloride. A blue color in the lower solvent layer indicates the presence of phenol in the test solution.

Diazotized Sulfanilic Acid Method.[10] *Reagents.* Diazotized Sulfanilic Acid.—This solution should be prepared 30 minutes before use. Acidify 100 ml. sulfanilic acid solution (1.91 g. of recrystallized sulfanilic acid, $NH_2C_6H_4SO_3H.H_2O$, dissolved in water and made up to 250 ml.) with 20 ml. of 25 per cent sulfuric acid. Add with a swirling motion, a few ml. at a time, 100 ml. of sodium nitrite solution (1.2 g. of sodium nitrite, $NaNO_2$, dissolved in water and made up to 250 ml.). Place the mixture in cracked ice or in a refrigerator for 30 minutes before using.

Sulfuric Acid Solution.—Use 25 per cent by volume of 1.84 specific gravity sulfuric acid. This solution must be carefully prepared because the final mixture must be definitely alkaline.[10a]

Sodium Hydroxide Solution.—Dissolve 8 g. of reagent sodium hydroxide in 92 ml. of water to give an 8 per cent solution by weight.

Procedure. Prepare phenol standards for comparison as detailed in the Gibbs' method and dilute to 100 ml. as before. Take adequate aliquots of the diluted test solution and transfer to Nessler tubes. Dilute to 100 ml. Add to each sample and standard in succession 10 ml. of diazotized sulfanilic acid solution. Stopper with clean dry rubber stoppers and tilt the rack holding the Nessler tubes twice to a horizontal position. Remove the stoppers and add 5 ml. of the 8 per cent by weight solution of sodium hydroxide to each tube in succession. Restopper the tubes with clean dry rubber stoppers and tilt the rack 10 times to a horizontal position to insure thorough mixing. After waiting 30 minutes for the color to reach its maximum intensity, read against a white background.

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[10] M. T. Hanke and K. K. Koessler, *J. Biol. Chem.*, *50*, 235 (1922).

[10a] *Standard Methods of Water Analysis, Am. Pub. Health Assoc.* (8th ed.), 1936.

Other methods for the determination of phenols and phenolic bodies are (1) the reduction of a phosphotungstic-phosphomolybdic acid reagent,[11,12] (2) the formation of highly colored compounds with diazotized *p*-nitroaniline,[13] and (3) by the use of nitrous acid with high concentrations of phenol.[14,15] Other methods are detailed by Levy.[16]

Determination of Phenol in the Presence of Other Phenols.[17] The method depends on the fact that cresols and higher phenols, in short, all phenolic substances in which the phenol hydrogen is not replaced, are not oxidized by a chromium trioxide-concentrated sulfuric acid mixture, while phenol is quantitatively broken down. The figure for phenol is obtained from the difference between that for all the phenolic bodies present simulating phenol in the diazotized sulfanilic acid reaction, and that obtained after the phenol has been destroyed. The standard for the determination is a phenol solution of known concentration treated in exactly the same manner as the unknown is treated.

Reagent. Prepare a saturated solution of chromium trioxide in sulfuric acid by placing twice the quantity of chromium trioxide, CrO_3, that will go into solution in a glass-stoppered bottle, and adding sulfuric acid. Shake from time to time over a period of several days and the solution is then ready for use.

Procedure. Use Kjeldahl distillation setups with 500-ml. flasks and 250-ml. graduated cylinders for receivers. Divide the test sample into 250-ml. portions and place in the flasks. When smaller amounts of sample are being used, they can be diluted to a known extent and an aliquot part taken for the analysis. Add 3 ml. of concentrated sulfuric acid to the contents of each flask. This is to render volatile all of the phenol. Then connect the flasks to the condensers by means of the Kjeldahl traps and place the cylinders in position to receive the distillates. Apply heat and catch 240 ml. of distillate in each case. Now put aside these distillates while the flasks and condensers are cleaned and rinsed with distilled water. Return the portions of the distillate to their respective flasks. To the first, add 10 ml. of the chromic acid solution prepared as directed above and to the second, add 10 ml. of concentrated sulfuric acid. Connect the flasks to the condensers and apply such heat as will bring the contents of each to the boiling point in 40 to 45 minutes. As soon as the boiling point is reached, remove the flames. Let the contents of

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[11] O. Folin and W. Denis, *J. Biol. Chem., 22,* 305 (1915).

[12] O. Folin and V. Ciocalteu, *J. Biol. Chem., 73,* 627 (1927).

[13] R. C. Theis and S. R. Benedict, *J. Biol. Chem., 61,* 67 (1924).

[14] R. M. Chapin, *Ind. Eng. Chem., 12,* 771 (1920).

[15] R. W. Stoughton, *J. Biol. Chem., 115,* 293 (1936).

[16] L. F. Levy, *J. South African Chem. Inst.,* 1939; *Analyst, 65,* 430 (1940).

[17] J. N. Miller and O. M. Urbain, *Ind. Eng. Chem., Anal. Ed., 2,* 123 (1930).

the flasks stand hot for 30 minutes. During this time, if sufficient care has been taken in bringing the solutions just to the boiling point, no more than a few drops of distillate will have passed over, most of the steam formed having condensed in the bulbs of the steam traps. Following the period of standing, apply the full flame and collect 225-ml. portions of distillate.

The second cylinder now contains all of the phenolic bodies simulating phenol plus the phenol. The first cylinder contains no phenol but all the other similar bodies. The difference between the contents of the two graduates in terms of a standard phenol solution which has received the same treatment as the second portion will be the phenol content of the sample.

Colorimetric determinations with diazotized sulfanilic acid may be made on aliquot portions of the distillates.

2. Cresols and Cresylic Acid

Cresols are used industrially in the manufacture of synthetic resins, explosives, and as preservatives, fumigants, disinfectants, and solvents. Cresol itself is a mixture of *o*-, *m*-, and *p*-cresol, $CH_3C_6H_4.OH$, obtained from coal tar and it generally contains a small percentage of phenol. Cresylic acid is the term used commercially to designate a mixture of phenols from coal tar, which boils from about 205° C. upwards. Creosote oil is the coal tar product obtained by distillation of coal-gas tar or coke-oven tar. Lysol, a trade-marked product, is essentially equivalent to the U. S. P. saponated solution of cresol, that is, cresol suspended in a linseed oil soap.

Cresol distills in the range of 195–205° C. and has a specific gravity of about 1.030–1.038 at 25/25° C. It varies in color from a colorless to a yellowish, pinkish, or brownish-yellow liquid with a phenolic odor. The color becomes darker with age and exposure to light. One part is soluble in about 50 parts of water. It is miscible with alcohol, benzene, ether, and petroleum ether and is also soluble in sodium and potassium hydroxide solutions.

The physiological response of the cresols is similar to phenol. The toxic effects resemble those of phenol but *o*- and *p*-cresol are more poisonous than phenol. The chief symptoms are irritation, coloration, and erosion of the skin and mucous membranes, and nephritis. A maximum allowable concentration of 5 parts per million has been suggested in California.

The cresols respond to many of the tests for phenol. They may be estimated by the bromide-bromate method detailed for phenol and may be calculated as phenol.[18]

The reaction that the cresols undergo is probably

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[18] R. D. Scott, *Ind. Eng. Chem., Anal. Ed., 3,* 67 (1931).

$$CH_3C_6H_4OH + 4Br_2 \longrightarrow CH_3C_6HBr_3OBr + 4HBr$$

$$CH_3C_5HBr_3OBr + 2KI + 2HCl \longrightarrow CH_3C_6HBr_3OH + 2KCl + HBr + I_2$$

The net result is 6 mols of bromine for 1 mol of cresol, which is similar to the reaction taking place for phenol. While these reactions may go to practical completion with *m*-cresol, with *o*- and *p*-cresol it is probable that the first reaction does not go to completion and the tribromo-oxybromotoluene compounds formed may not be completely reduced, in which event high values may result. It is probable also that there is a considerable formation of dibromo-oxybromotoluene compounds with incomplete reduction to dibromocresols, with resulting low values when calculated as tri- compounds. In addition there may be some conversion of tribromocresols into tribromophenol.

The bromide-bromate method for mixed cresols provides a method yielding approximately quantitative results when calculated to a phenol basis. The result can be ascertained more accurately by the relationship that 1 ml. of 0.1 *N* sodium thiosulfate solution is equivalent to 0.0018 g. of cresol.

3. Resorcinol

Resorcinol, $C_6H_4(OH)_2$, *m*-dihydroxybenzene, commercially termed resorcin, is used industrially in tanning, in the manufacture of explosives, dyes, and other organic chemicals, in cosmetics, in photography, and medicinally. It is a solid consisting of white, needle-like crystals which have a characteristic odor and become pink on exposure to air. Resorcinol has a specific gravity of 1.272; melts at 109–111° C.; and boils at 280° C. but is volatile at lower temperatures and is slightly volatile with steam.

Resorcinol may cause dermatitis in workers exposed to it, especially some who are hypersensitive.[19] These persons are affected by even the slightest trace of the substance. Deaths have resulted from dermatitis caused by resorcinol which was a component of medicinals.[20]

Resorcinol may be detected by many of the tests given for phenols and cresols. It may be detected by the reverse of the test for formaldehyde. It can be estimated by the Koppeschaar bromide-bromate method for phenol.[21] In this case 6 mols of bromine are equivalent to 1 mol of the compound, thus 1 ml. of 0.1 *N* sodium thiosulfate solution is equivalent to 0.001834 g. of resorcinol.

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[19] L. Schwartz, *U. S. Pub. Health Service, Bull.* 249 (1939).

[20] W. D. McNally, *Medical Jurisprudence and Toxicology,* Saunders, Philadelphia, 1939.

[21] C. M. Pence, *Ind. Eng. Chem., 3,* 820 (1911).

Koppeschaar Method for Phenols and Aromatic Amines.[22] This method depends upon the bromination of phenols and aromatic amines by an excess of potassium bromide-potassium bromate solution, the excess being estimated by the use of potassium iodide and standard thiosulfate solution. The bromine for the bromination is supplied by the interaction of potassium bromate with the bromide in the presence of sufficient hydrochloric acid:

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 6Br + 3H_2O + 6KCl$$

Transfer an aliquot or if necessary the entire sample collected by some appropriate method of trapping, such as a midget impinger, to a 250-ml. volumetric flask, and dilute to volume. If the substance is an amine, dilute hydrochloric acid may be used in the trapping solution; if it is a phenol or a sulfonic acid, dilute sodium hydroxide solution may be used to preserve the compound.

Pipette a 25-ml. aliquot of the sample solution into a 500-ml. iodine flask (Fig. 120) and add 25 ml. of 0.2 *N* bromide-bromate solution, 75 g. of potassium bromide, KBr, and 5.6 g. of potassium bromate, $KBrO_3$, dissolved in water and made up to 1 liter. Add 50 ml. of water, then 5 ml. of concentrated hydrochloric acid and stopper the flask at once. Shake for 1 minute and then allow to stand with occasional agitation for a definite interval, which varies with the ease of bromination of the compound analyzed. These times are tabulated in Table 30.

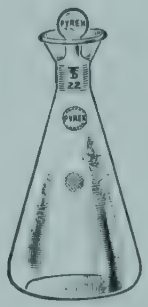

Fig. 120. Iodine flask. (*Courtesy Corning Glass Works*)

Cool the flask under tap water or in an ice bath or refrigerator and pour 5 ml. of 40 per cent potassium iodide solution into the flare trough of the iodine flask. Partially dislodge the stopper and allow the iodide solution to flow into the flask without loss of bromine. Restopper the flask and shake thoroughly. Remove the stopper and wash the neck of the flask and the stopper with water. Titrate the free iodine, which is equivalent to the excess bromine, with 0.1 *N* sodium thiosulfate, using 1–2 ml. of 1 per cent starch solution as indicator.

Run a blank determination using 25 ml. of the bromide-bromate solution and 50 ml. of water, and follow the procedure as outlined.

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[22] A. R. Day and W. T. Taggart, *Ind. Eng. Chem., 20,* 545 (1928).

4. Pyrocatechol

Pyrocatechol, *o*-dihydroxybenzene, also known as catechol, is used in the dyeing of furs and hair and in photography. It is a white crystalline solid which discolors rapidly in air and light. It melts at 104–105° C., has a specific gravity of 1.344, and boils at about 240–245° C.; it sublimes easily and is volatile with steam. It causes poisoning and dermatitis, especially in people who are supersensitive to it.

Determination. This method depends upon the production of a violet color when a reagent containing ferrous sulfate and Rochelle salt is added to a solution containing catechol.[23–25]

TABLE 30

Bromination Period

Substance	Solvent	Dilution, ml. of H_2O	Bromination period, min.	Bromine equivalent
Phenol	NaOH	50	5–30	6
p-Chlorophenol	NaOH	100	30	4
o-Nitrophenol	NaOH	50	30	4
m-Nitrophenol	NaOH	50	5–30	6
p-Nitrophenol	NaOH	50	5–30	4
2,4-Dinitrophenol	NaOH	50	30	2
Salicylic acid	NaOH	50	30	6
m-Cresol	NaOH	50	1	6
Resorcinol	H_2O	100	1	6
β-Naphthol	NaOH	None	15–20	2
Aniline	HCl	50	5–10	6
p-Chloroaniline	HCl	50	10	4
o-Nitroaniline	HCl	100	30	4
m-Nitroaniline	HCl	50	30	6

Procedure. To 1 ml. of a sample containing about 0.2 mg. of the phenol, add 2 ml. of a freshly prepared reagent containing 0.1 per cent of ferrous sulfate and 0.5 per cent of sodium potassium tartrate. Add 10 ml. of 10 per cent ammonium acetate solution to buffer the mixture at a pH of 7.6 after dilution to 100 ml. The addition of 1 ml. of concentrated ammonia gives a pH of 8 and maximum intensity. Compare with standards treated the same way.

Pyrogallol, gallic acid, tannic acid and protocatechuic acid can also be estimated by this method.

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[23] C. A. Mitchell, *Analyst, 48,* 2 (1923).
[24] C. M. Pence, *Ind. Eng. Chem., 3,* 820 (1911).
[25] S. Glasstone, *Analyst, 50,* 49 (1925).

5. Hydroquinone

Hydroquinone, *p*-dihydroxybenzene, also known as quinol, is used in the photographic industry as a reducer and developer. It is a white crystalline solid with a specific gravity of 1.332; it melts at 170–171° C. and boils at 285–287°C. It becomes brown upon exposure to air and light both in the solid form and in solution. Hydroquinone is said to cause keratitis and discoloration of the conjunctiva among laborers exposed to steam or dust during its manufacture and use.[26]

Hydroquinone may be detected and estimated by use of the reactions listed in Table 31.

6. Pyrogallol

Pyrogallol, $C_6H_3(OH)_3$, trihydroxybenzene, is used fairly widely in industry. It is used in the dyeing of fur and hair, in staining leather, in photography, in marking inks, and as a mordant for wood. It is a white crystalline solid which becomes grayish on exposure to air and light. It has a specific gravity of 1.45, melts at 131–133° C., boils at 309° C., and sublimes when carefully heated.

Pyrogallol can be absorbed by the skin. The principal symptom of poisoning attributable to pyrogallol is its effect on the red blood corpuscles. These lose their hemoglobin and shrink.[27] Symptoms exhibited in severe poisoning are urinary disturbances, headache, cyanosis, chills, vomiting, diarrhea, and death. Pyrogallol is not only a systemic poison but is also a skin irritant and causes dermatitis.

Pyrogallol may be detected by the use of the reagents listed in Table 31. It gives a violet-brown color with nitrous acid and concentrated sulfuric acid.

Osmium Tetroxide Method.[27a] Pyrogallol combines with osmium tetroxide to form a compound which is reddish violet in dilute solution and almost black when concentrated. The reaction is extremely sensitive and is capable of detecting as little as 1 part of pyrogallol in 2 million parts of water.

Reagent. Dissolve 1 g. of osmium tetroxide, OsO_4, in water and dilute to 100 ml. For the test dilute 1 part of this 1 per cent solution with 10 parts of water.

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[26] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939).

[27] W. D. McNally, *Medical Jurisprudence and Toxicology,* Saunders, Philadelphia, 1939.

[27a] C. A. Mitchell, *Analyst, 49,* 162 (1924).

Procedure. Transfer 1 ml. of the test solution to a Nessler tube of 100-ml. capacity, if the test solution is of the order 0.1 per cent concentration, and dilute to 100 ml. with water. Otherwise use an appropriate aliquot and dilute to 100 ml. Add 1 ml. of the diluted osmium tetroxide reagent and allow to stand for 5 minutes, after which period compare with a standard treated the same way at the same time.

The standard for comparison may be made by dissolving 0.1 g. of pure pyrogallol in 100 ml. of water. One ml. of this solution is treated in the same way as the unknown.

Gallic acid and catechol react in a similar fashion and can be estimated in the same way by this method. Phenol, salicylic acid, phloroglucinol, and resorcinol do not give this reaction.

It is necessary that the solution should not be acid. A slight excess of alkali does not affect the result. The pH of the solution may be adjusted by the addition of 1 ml. of 0.1 *N* sodium carbonate solution.

B. AROMATIC AMINO COMPOUNDS

1. Aniline

Aniline is an intermediate for the manufacture of many organic compounds, such as dyes, drugs, rubber accelerators, and resins, and in the formulation of inks, paints and varnishes, shoe polish, perfumes, and the vulcanization of rubber goods. It is also used in the leather industry.

Aniline is an oily liquid, colorless when recently distilled but becoming brown on exposure to light and air. It has a characteristic, peculiar odor and a burning taste. It boils at 184–186° C. and is volatile with steam. It has a specific gravity of 1.022 at 20/20° C. and a refractive index of 1.5863 at 20° C.; it solidifies at —6° C.; is inflammable and has a flash point of 70–76° C. About 3.5 g. dissolves in 100 ml. of water. It is miscible with alcohol, benzene, and most other common organic solvents. It combines with acids to form well-characterized salts.

a. Physiological Response

Poisoning from aniline may occur by absorption through the skin as well as by inhalation of vapors and dust, and by swallowing dust with saliva or food. Clothes wet with spilled aniline are often the mode of entrance to and then through the skin. Aniline and its immediate homologues are blood and nervous system poisons.[28]

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[28] A. Davis, *J. Ind. Hyg., 3,* 57 (1922).

The symptoms exhibited by persons suffering from acute aniline poisoning may be summarized as pallor followed by cyanosis, especially of the lips and finger tips, weakness, somnolence, irritability, mental confusion, headache and vertigo, unsteady gait, muscular tremor, convulsions, and death. The symptoms that occur in chronic cases of aniline poisoning are eczema, anemia, weak pulse, brownish discoloration of the blood and urine.

The maximum concentration that can be tolerated for 60 minutes without serious symptoms is 100–150 parts per million.[29] The recommended maximum safe working concentration is 5 parts per million but workers should be under medical supervision even at this concentration.

Aniline causes blood disturbances.[30] The brownish coloration of the blood is due to the formation of oxidation products of aniline. Any *p*-aminophenol formed may be detected in the urine. Aniline is also excreted in part as the ethereal sulfate.

The toxicity of benzene derivatives is discussed by Smyth,[31] and that of the aromatic and amino compounds by von Oettingen.[31a]

b. Detection

Sampling. Aniline vapor in air may be trapped by passing the air through an efficient bubbler containing 10 per cent sulfuric acid solution, or through traps containing cotton or beads wet with this reagent. If beads or cotton are used, transfer the cotton or beads to a funnel arranged so that the beads and cotton will not wash through, and wash thoroughly with water, catching the washings in a flask. If a quantitative determination is to be made wash until the beads or cotton are free of acid. A fritted bubbler containing sulfuric acid (1:100) is recommended for trapping aniline to be estimated by the hypochlorite-phenol method described below.

Carbylamine Reaction. If necessary distill, otherwise almost neutralize the solution. Add 3 drops of chloroform and 2 ml. of an alcoholic potash solution to a 10-ml. aliquot. Heat for a moment. The repulsive odor of phenylisocyanide is indicative of aniline. The addition of bromine water to another portion of the sample will precipitate flesh-colored tribromoaniline.

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[29] R. R. Sayers, *International Critical Tables* (Vol. II), McGraw-Hill, New York, 1927.

[30] F. P. Underhill, *Toxicology,* Blakiston, Philadelphia, 1928.

[31] H. F. Smyth, *J. Ind. Hyg., 13,* 87 (1931).

[31a] W. F. von Oettingen, *U. S. Pub. Health Service, Bull. 271* (1941).

c. Determination

Colorimetric Estimation by Means of Hypochlorite.[32] This method is based on the production of a purplish-violet coloration, which later changes to dirty red, when a hypochlorite solution is added to an aqueous solution of aniline.

The aniline vapors may be collected as noted above or by bubbling 10 liters of the air to be examined through a suitable absorption bulb containing 10 ml. of water acidified with sulfuric acid.

Reagent. Calcium Hypochlorite Solution.—Prepare a calcium hypochlorite solution, the available chlorine content of which is 0.1 per cent. from a stock solution. The stock solution may be made by shaking thoroughly for 10 minutes 20 g. of fresh commercial chlorinated lime with 100 ml. of water and filtering. This is a solution whose available chlorine content is approximately 3 per cent. Obtain the true available chlorine content iodometrically and dilute a proper aliquot to give the 0.1 per cent available chlorine solution. This stock solution should not be prepared from a chlorinated lime which has lost much of the available chlorine it originally had, since it might leave too much calcium in the final reagent and thus cause a precipitate or turbidity when the excess alkali is added.

Procedure. Carry out a preliminary test on the solution to be examined to ascertain the approximate amount of aniline present. If this indicates that its concentration is more than 1 part of aniline in 200,000 of solution. dilute the solution with water so as to make it fall within the range of the standards used, that is, from 1 part of aniline in about 285,000 of solution to 1 part in 2,000,000. Mix 20 ml. of this solution with 1 ml. of calcium hypochlorite solution with an available chlorine content of 0.1 per cent. Use pipettes with comparatively large outflow openings so as to consume as little time as possible for the addition of the reagents. This permits the test solutions and the standards to be made up at almost the same time. Allow to stand for 2 minutes. Add 1 ml. of N sodium hydroxide solution, mix, and allow to stand for 10 minutes. using only 5 minutes for the standard containing the smallest amount of aniline.

Compare the color of this solution with those of standards obtained by treating known amounts of standard aniline solution in a similar fashion. Mix the reagents and carry out the readings in the same tube. Narrow-form 50-ml. Nessler tubes are convenient. The mixing of the unknown solution and the standards with the reagents may be done nearly simultaneously with the aid of bulbed glass rods, by means of which it is comparatively easy to mix thoroughly the contents of four or five tubes practically at the same time.

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[32] E. Elvove, *Ind. Eng. Chem.*, *9*, **953** (1917).

Prepare the standards from a stock solution of pure aniline by dissolving 1 g. of aniline in water and diluting to 1 liter. Dilute 10 ml. of this solution to 1 liter. Then prepare standards containing 0.0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.07 mg. of aniline by taking proper aliquots and diluting to 20 ml.

Instead of diluting the solution to be examined, one may also prepare a set of standards with correspondingly higher aniline concentrations. For example, a series of standards may be prepared having ten times the concentrations given above, containing 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 mg. respectively. In using such a higher series of standards, it is more advantageous to adopt a little longer interval than 10 minutes for the tube to stand before being read, when the higher end of the standards are the ones to be used for the comparison.

Hypochlorite-Phenol Method. This method depends on the formation of the hydrochlorite complex of aniline and its conversion to a permanent deep-blue dye by the addition of ammonia and a dilute solution of phenol. This test is more sensitive than the hypochlorite reaction. It has been adopted as the official British[33] method for detecting and estimating aniline vapors in air.

The apparatus used for this test has been described in the sections devoted to the hand pump (page 33) and to carbon disulfide (page 329).

Preparation of Reagents. Calcium Hypochlorite Solution.—Warm 5 g. of calcium hypochlorite, containing not less than 25 per cent of available chlorine, with 100 ml. of water at 50–60° C. with constant shaking. Filter while hot.

Phenol Reagent.—Dissolve 5 g. of phenol in 100 ml. of an ammonia solution prepared by diluting 50 ml. of ammonia, specific gravity 0.880, to 1 liter.

Preparation of Standard Colors. Toluidine Blue Standards.—Dissolve 0.28 g. of well-ground Toluidine Blue dye, commonly used as a stain for microscopic work, in cold water. Shake well until dissolved and dilute to exactly 1 liter. Weigh out the portion accurately. The dye may take some time to go into solution.

The series of standards is then prepared by diluting the following aliquots of 0.028 per cent dye solution to 100 ml.

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[33] *Dept. Sci. Ind. Research Brit., Leaflet 11* (1939).

Standard No.	Volume of 0.028% dye solution diluted to 100 ml.
1	3.5 ml.
2	7.0 ml.
3	10.0 ml.
4	15.0 ml.
5	20.0 ml.

Since the strength of commercial Toluidine Blue may vary, the standards may be checked against a copper sulfate-potassium permanganate solution. Grind the dyestuff thoroughly and prepare the 0.028 per cent dye solution as directed above. Make the No. 3 standard.

Prepare a copper sulfate-potassium permanganate check color by dissolving 30 g. of copper sulfate, $CuSO_4.5H_2O$, in water and diluting to 100 ml. Add to this solution 1.2 ml. of a freshly prepared potassium permanganate solution, 0.3 g. of potassium permanganate, $KMnO_4$, dissolved in water and made up to 100 ml.

Compare standard No. 3 with the copper sulfate-potassium permanganate check by observing the colors in tubes of the same bore side by side. The depth of color in the two tubes should be identical. If any difference is observed, the strength of the original 0.028 per cent Toluidine Blue solution should be adjusted until the new standard No. 3 matches the check color. The other standards may then be prepared from the adjusted Toluidine Blue solution as described.

Procedure. Transfer 10 ml. of 1 per cent hydrochloric acid, 25 ml. of concentrated hydrochloric acid diluted to 1 liter with water, to the side-arm bubbler. Connect the hand-pump apparatus and the rest of the train. Draw 5 strokes of the pump very slowly, using about 10 seconds for each stroke, in the atmosphere to be tested, as a preliminary test. The complete test takes about half an hour but the bulk of the color develops in the first 10 minutes. Hence concentrations up to 1 part in 15,000 (67 parts per million) can be roughly estimated in the first 10 minutes.

After the preliminary test, which is completed as described below, further tests can be made in order to obtain a more accurate result by using a suitable number of strokes.

	No. of strokes			
Concentration, parts by vol.	1	3	5	10
	Standard No.	Standard No.	Standard No.	Standard No.
1 in 5,000	3–4			
1 in 10,000	2	4		
1 in 15,000		3–4	5	
1 in 20,000	1	3	4	
1 in 30,000		2	3	5
1 in 50,000			2	3–4
1 in 100,000			1	2
1 in 200,000				1

Detach the bubbler from the train, after the desired number of strokes have been made. Add 2 drops of the hypochlorite reagent, allow the mixture to stand for 5 minutes, and then bring to boiling. Add 5 ml. of the phenol reagent and allow the mixture to stand for 15 minutes. If any aniline is present, a blue color will develop. Transfer the test solution to a small Nessler tube and compare the depth of color against the standards in similar Nessler tubes. Colorimeters may be used if available.

When a color less than standard No. 1 is obtained with 10 strokes of the pump, indicating a concentration of less than 5 parts of aniline per million of air, the number of strokes may be increased until this standard is reached. The actual concentration present may then be calculated by proportion from the figures given for a smaller number of strokes.

Titrimetric Estimation. Aniline may be estimated titrimetrically by the following modification of the bromide-bromate method. Aniline is bromated to form tribromoaniline.

Procedure.[34] Transfer 25 ml. of an approximately 0.01 *M* solution of aniline to a flask. Add 25 ml. of 0.1 *N* potassium bromate solution, 0.5 g. of potassium bromide, and 5 to 10 ml. of 4 *N* sulfuric acid. Stopper the flask and allow to stand for 5–10 minutes. Add 1 g. of potassium iodide, and titrate with 0.1 *N* sodium thiosulfate solution, while stirring thoroughly. Use 1 per cent starch solution as indicator, adding the starch towards the end of the titration. The addition of a little chloroform at the end of the titration prevents the absorption of some iodine by the tribromoaniline. One ml. of 0.1 *N* bromine is equivalent to 0.00155 g. of aniline.

Aniline may also be estimated by direct titration with standard bromine solution, using indigo carmine as the indicator. The indicator becomes colorless with an excess of bromine.[35]

2. *Toluidine*

The principal commercial toluidine is the ortho compound. It is used in the manufacture of various dyes and explosives; for printing textiles blue-black, and other dyeing uses; and as an intermediate in the manufacture of organic compounds.

It is a reddish-brown liquid which boils at 200–202° C.; has a specific gravity of 1.008 at 20/20° C.; a refractive index of 1.5688 at 20° C.; and a flash point of 87° C. It is slightly soluble in water and is soluble in alcohol, ether, and dilute acids.

Its main portal of entry into the body is the respiratory tract. The symptoms produced by poisoning from this compound are headache, weakness, difficulty in breathing, cyanosis, convulsions, psychical disturbances, air hunger, and marked irritation of the renal organs. A concentration of 90–140 parts of the vapor per million of air is the maximum concentration endurable for 60 minutes without serious disturbance. Concentrations of 6 to 23 parts per million are endurable for exposure of several hours without serious disturbance.[36] The recommended maximum allowable concentration is 5 parts per million parts of air.

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[34] I. M. Kolthoff and N. H. Furman, *Volumetric Analysis,* New York, 1929.

[35] A. V. Pamfilow and V. E. Kisselva, *Z. anal. Chem., 72,* 100 (1927).

Tests for the detection of toluidine are given in Table 31. Quantitative estimation may be made by means of the bromide-bromate method (page 705).

3. Xylidine

Xylidine, $(CH_3)_2C_6H_3NH_2$, *C*,*C*-dimethylaniline, has been used for the blending of gasoline. The commercial product, which is prepared by the reduction of nitroxylene, is probably a mixture of the six possible isomers, some 40 to 60 per cent being 4-amino-*m*-xylene and 10 to 20 per cent being 2-amino-*p*-xylene. These isomers are used for the manufacture of azo dyes.

The toxicity and potential dangers of xylidine as compared with those of aniline were studied by von Oettingen and co-workers.[37] Xylidine is a toxic material which may cause injury to the blood and especially to the liver, without necessarily causing warning signs such as cyanosis, headache, and dizziness. This makes xylidine a more insidious poison than aniline. Sufficient quantities of xylidine may be absorbed through the skin to cause severe and possibly fatal poisoning.

Determination

The concentration of xylidine in air may be estimated by the liberation of ammonia or by the formation of a dye. A spectrophotometric method is described by Svirbely and Peterson.[37]

Ammonia Method. Svirbely and Alford[37] estimate xylidine by a variation of the Koch-McMeekin method for protein. Bubble 2 liters of xylidine vapor-air mixture slowly through a midget impinger containing 20 ml. of water and 2 drops of sulfuric acid (1:1). Evaporate till fumes appear, cool, add 1 drop of 30 per cent hydrogen peroxide solution, and allow to cool again. Dilute to 35 ml. with water, add 15 ml. of Nessler's reagent (see page 364), and after 3 to 5 minutes read in a photoelectric colorimeter using a filter with maximum transmission at 425 mμ. Prepare a calibration curve and run a blank as detailed.

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[36] Y. Henderson and H. W. Haggard, *Noxious Gases*, Reinhold, New York, 1927.

[37] W. F. von Oettingen, P. A. Neal, R. F. Sievers, J. L. Svirbely, A. R. Monaco, B. L. Horecker, H. Yagoda, T. R. Sweeney, D. C. Peterson, W. C. Alford, V. B. Hauff, and H. Gay, *U. S. Pub. Health Service, Natl. Inst. Health Bull. 188* (1947).

Dye Method. After diazotization xylidine will form a dye by coupling with H acid, 1-amino-8-naphthol-3,6-disulfonic acid. Draw a sufficiently large volume of air containing xylidine through a midget impinger containing 20 ml. of water acidified with 1 drop of sulfuric acid (1:1) to give about 5 micrograms of material.

By adequate dilution of a primary standard consisting of 1 g. of xylidine in a liter of 0.1 per cent sulfuric acid, prepare a series of standards containing 0, 5, 10, 25, and 50 micrograms of xylidine per 20 ml. of water acidified with 1 drop of sulfuric acid (1:1).

To both standards and unknown, add 2 drops of 10 per cent sodium nitrite solution, mix, and allow to stand for 2 minutes. Add 2 ml. of a solution of dipotassium hydrogen phosphate, prepared by dissolving 85 g. of anhydrous K_2HPO_4 in water and diluting to 100 ml. Mix, add 0.3 ml. of a 1 per cent aqueous solution of H acid, and allow to stand for 5 minutes away from strong light. In the presence of xylidine a purplish-red color is formed. Compare the unknown and standards immediately after by use of Nessler tubes or a Duboscq-type colorimeter.

4. Dimethylaniline

Dimethylaniline, $C_6H_5N(CH_3)_2$, is a yellow liquid which boils at 192.5–193.5° C., has a density of 0.9557 at 20/4° C., and has a refractive index of 1.5582. It is used in the manufacture of tetryl. It is considered highly toxic and the recommended maximum allowable concentration for daily 8-hour exposures is 5 parts of dimethylaniline per million parts of air.

Collect this material in a fritted-glass bubbler containing alcohol at a sampling rate of 0.5 to 1 liter per minute. Treat the sample solution with nitrous acid to form the colored nitroso compound. Estimate colorimetrically against standards treated the same way. An alternative collection medium is sulfuric acid (1:100).

5. Diphenylamine

Diphenylamine, $(C_6H_5)_2NH$, is a colorless crystalline solid, melting in the pure state at 53° C. and boiling at 302° C. It is very slightly soluble in water but is very soluble in alcohol, ether, methyl alcohol, benzene, and similar solvents. It is used in the manufacture of smokeless powder.

Diphenylamine may occur as a vapor. A recommended sampling procedure is to trap the air containing it by use of a midget impinger containing sulfuric acid (1:100). An alternative sampling procedure is to use a fritted bubbler also containing sulfuric acid (1:100).

Diphenylamine gives a purple color when added to ferric ammonium sulfate in sulfuric acid. This is the basis of a colorimetric method. With alcohol a blue solution is obtained.

6. *p-Phenylenediamine*

p-Phenylenediamine is used widely as a fur and hair dye. It is also used as an accelerator in the rubber industry but this use is diminishing. This diamine is an intermediate in the production of dyes.

p-Phenylenediamine, $C_6H_4(NH_2)_2$, is a colorless crystalline solid when pure but rapidly darkens and turns brown on exposure to air. It melts at 145–147° C. and boils at 267° C. This compound with other compounds such as *p*-aminophenol hydrochloride, which yield dyes when treated with sodium hydroxide and hydrogen peroxide solutions, are sometimes marketed under the name "Ursol."

a. Physiological Response

p-Phenylenediamine is poisonous. It is a blood poison producing edema, salivation, eczema, and other unpleasant effects.[38,39] It produces exophthalmia, completely altering the tissues of the eyes. In a study made by Cox[38] on the probable cause of dermatitis in 216 cases attributable to wearing furs, over 45 per cent were due to *p*-phenylenediamine and another 12.5 per cent were due to *m*-phenylenediamine. In the rubber industry *p*-phenylenediamine ranked next to hexamethylenetetramine as a principal cause of dermatitis among workers.[40,41]

In the oxidation of *p*-phenylenediamine, the first step is the formation of quinone diimine, $NH{:}C_6H_4{:}NH$, which has a sharp pentrating odor and produces violent local irritations of the mucous membranes and skins of sensitive individuals. By breathing the dust of *p*-phenylenediamine, quinone diimine is formed in the respiratory tract.[42] There it may be oxidized to a complex substance known as Bandrowski's base, which has less-irritating powers.

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[38] H. E. Cox, *Analyst, 58,* 738, 743 (1933).

[39] W. D. McNally, *Medical Jurisprudence and Toxicology*, Saunders, Philadelphia, 1939.

[40] L. Schwartz, *U. S. Pub. Health Service, Bull. 215* (1934).

[41] R. S. Quinby, *J. Ind. Hyg., 8,* 103 (1926).

[42] L. Schwartz, *U. S. Pub. Health Service, Bull. 229* (1936).

b. Detection and Determination

p-Phenylenediamine can be detected by the formation of indamine by a reaction with aniline in the presence of ferric chloride or some other appropriate oxidizing agent, such as potassium persulfate.[43,44]

Procedure. To 10 ml. of the test solution add 3 drops of 1 per cent aniline hydrochloride solution and 3 drops of 1 per cent ferric chloride solution. The maximum intense green-blue color is produced at a pH of 4.5. Quantitative results can be obtained by comparison with standards and the use of a colorimeter.

Indophenol Reaction. To 10 ml. of the test solution add 3 drops of a 1 per cent solution of phenol and 3 drops of sodium hypochlorite solution. An intense violet color is formed.

Callan and Henderson Method.[45] On the addition of p-phenylenediamine to a solution of hypochlorite containing sodium carbonate, the amount of hypochlorite, or available chlorine, removed from solution is proportional to the amount of p-phenylenediamine present in accordance with the equation:

$$C_6H_4(NH_2)_2 + 6Cl \longrightarrow C_6H_4(NCl)_2 + 4HCl$$

The amount of available chlorine so removed is readily determined by means of a standard sodium arsenite solution.

Reagents. Prepare a stock solution of sodium hypochlorite by diluting 50 ml. of commercial hypochlorite solution containing 12–15 per cent of available chlorine to 1 liter. Titrate 50 ml. of this solution with 0.1 *N* sodium arsenite solution, using starch-iodide paper as indicator.

Procedure. Dilute 100 ml. of the hypochlorite solution with an equal volume of cold water. Add about 1 g. of sodium carbonate and add slowly with constant stirring 10 ml. of the unknown solution containing the p-phenylenediamine dissolved in a slight excess of hydrochloric acid. The mixture should at this point give a strong reaction with starch-iodide paper, otherwise the procedure must be repeated using a larger amount of hypochlorite solution or a lesser amount of p-phenylenediamine solution. On the addition of the p-phenylenediamine solution, benzoquinonedichloroimide is rapidly precipitated as an almost white substance. Titrate the turbid mixture without filtration with 0.1 *N* sodium arsenite solution, using starch-iodide paper as an external indicator, the end point being very sharply indicated by the disappearance of the blue

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[43] F. Feigl, *Spot Tests,* Elsevier, New York, 1939.

[44] H. E. Cox, *Analyst, 58,* 738 (1933).

[45] T. Callan and J. A. R. Henderson, *J. Soc. Chem. Ind., 38,* 408T (1919).

color on spotting out on the indicator paper. At the end of the titration the solution should still be distinctly alkaline. The total time of the titration should only be a few minutes.

The difference in volume of 0.1 *N* sodium arsenite solution required for the titration of the sodium hypochlorite solution itself, and for the mixture of hypochlorite and diamine, is equivalent to the amount of active chlorine removed from the solution as benzoquinonedichloroimide, each ml. of 0.1 *N* arsenite solution corresponding therefore to 0.0018 g. of *p*-phenylenediamine. If very dilute diamine solutions are being tested, use much more dilute hypochlorite solution and titrate with 0.01 *N* sodium arsenite solution, 1 ml. of which will be equivalent to 0.00018 g. of *p*-phenylenediamine.[46]

This method can be used for *p*-nitroaniline, which is readily reduced to *p*-phenylenediamine by the cautious addition of zinc dust and hydrochloric acid. The mixture is filtered, neutralized with sodium carbonate, made up to volume, and an aliquot is analyzed as above.

It may also be used for *p*-aminoacetanilide after hydrolysis with hydrochloric acid.

Naphthylene-1,4-diamine can also be estimated by this method. Benzidine is another substance that can be determined.

With *p*-aminodiphenylamine the reaction proceeds as follows:

$$NH_2C_6H_4NHC_6H_5 + 4Cl \longrightarrow ClC_6H_4{:}NC_6H_5 + 3HCl$$

The analytical procedure is the same except that a large excess of sodium carbonate must be used.

p-Aminophenol must be estimated in *acid* solution. Add an excess of sodium hypochlorite solution. Aerate to drive off the excess available chlorine not combined as quinonechloroimide. Add potassium iodide and titrate with 0.1 *N* sodium thiosulfate solution.

7. Common Irritant Dyestuffs[46]

While the number of dyestuffs or intermediates which may be applied to furs is quite large, the following is a list of the more common and possibly irritant ones:

(1) *m*-Phenylenediamine
(2) *p*-Phenylenediamine
(3) 1,2,4-*m*-Tolylenediamine
(4) 1,3,4-*m*-Tolylenediamine
(5) *o*-, *m*-, *p*-Toluidine
(6) Pyrogallol
(7) Quinone
(8) Hydroquinone
(9) *p*-Aminophenol (Ursol-P.)
(10) Diaminophenol (Amidol)
(11) *p*-Methylaminophenol (Metol)
(12) Diaminodiphenylamine

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[46] H. E. Cox, *Analyst, 54,* 694 (1929).

All these substances are strong reducing agents and reduce silver nitrate solution; several are known as photographic developers, some of which cause irritation and blisters on the fingers of persons with sensitive skins. They also reduce Fehling's solution, with the production of various colors, but these colors are not sufficiently constant for test purposes for they are influenced by concentration and other substances which may be extracted from fur.

Identification Reactions. The following reactions all apply to aqueous solutions in concentrations of 1 in 10,000. They are distinctly visible at this concentration, and many of them at 1 in 100,000, some even at greater dilutions, especially if viewed in column in Nessler tubes. They are sufficient for identification of the substances named, although the colors are not definitely specific in all cases. It is best to confirm the reactions and not take one test as conclusive; thus, for instance, the yellow color with sodium nitrite solution is given by several other substances besides one of the commonest, *m*-phenylenediamine. Mixtures complicate the reactions. Care must be taken not to add too much reagent, especially when testing very dilute solutions.

In the case of test (4) in Table 31, it is important that the solutions should not contain any free acid, or chlorine may be liberated and a different reaction be obtained; the solution should be neutral or very slightly alkaline; any large excess of hypochlorite must be avoided, or the color of the reaction may be bleached. This test is not equally valuable in all cases; for example, the difference between the brownish-pink given by *m*-phenylenediamine or 1,2,4, *m*-tolylenediamine and the violet-blue of *p*-phenylenediamine and 1,3,4, *m*-tolylenediamine is distinctive, but, though the three toluidines give different colors when pure, it is not practicable to distinguish them in very dilute solution as extracted from fur.

In test (5) the solution should be distinctly acid with hydrochloric acid; this reagent, which is the familiar indole reagent of the bacteriologist, serves to distinguish *p*-phenylenediamine from *m*-tolylenediamine.

In test (6) about 2 drops of ferric chloride solution should be added to the neutral or faintly acid test solution, then hydrogen sulfide water, 1 ml. at a time, for a large excess may mask the color or liberate sulfur.

The reduction of Fehling's solution in the cold refers to the effect observed on adding 3 or 4 drops of mixed Fehling solution to 5 ml. of the solution to be tested, not to the reverse addition of a little of the solution to be tested to a relatively large volume of the Fehling solution in the ordinary sugar test. It is generally advisable to use boiled and cooled water to eliminate oxidation as far as possible, and the solutions should be fairly fresh.

Approximate estimations of the amount of any of these substances may be made colorimetrically by comparison with known solutions using the same volumes of reagents.

Extraction of Fur. Cut the fur from the skin as closely as possible and remove the fat with petroleum ether. Then extract with (1) boiled, cooled water and (2) 1 per cent acetic acid for at least 24 hours. All the solutions should be preserved from atmospheric oxidation as much as

TABLE 31

Reactions of Dyestuffs and Intermediates[46]

Substance	1 Dilute $NaNO_2$ added to cold	2 Excess of alkaline soln. naphthol added to 1	3 Bromine water	4 Phenol 5% soln. + 2 drops NaClO added to neutral solution
m-Phenylenediamine	Intense brownish yellow	Reddish brown	Slight white ppt.	Pink
p-Phenylenediamine	Slight brown (fades)	Brownish	Nil	Violet blue
1,2,4, *m*-Tolylenediamine	Orange	Intense red	Nil	Pink
1,3,4, *m*-Tolylenediamine	Brownish pink	Dirty yellow or brown	Very faint ppt.	Violet
p-Aminophenol	Slightly yellow	Fluorescent green afterwards brown	Nil	Blue
p-Aminodiphenylamine	Red	Yellow or brown	Brownish ppt.	Yellow
o-, *m*-, *p*-Toluidine	Nil	Bright red color or ppt.	White ppt.	Brown at first, *o*- and *m*- then become blue
2,4-Diaminophenol	Bright red	Brown	White ppt.	Red
Methyl *p*-aminophenol	Faint yellow	Slightly brown	Nil	Blue-violet develops slowly
Quinone	Nil	Slight reddish	Nil	Nil
Hydroquinone	Faint yellow	Red	Nil	Nil
Pyrogallol	Nil	Nil	Nil	Brownish

TABLE 31—*Continued*

Substance	5 Alcoholic soln. of *p*-dimethyl-aminobenz-aldehyde to acid soln.	6 Ferric chloride	7 H_2S water added to	8 Mercuric acetate soln.	9 KCN soln.	Remarks
m-Phenylenediamine	Bright yellow	Nil	Nil			
p-Phenylenediamine	Red	Violet	Intense violet	...	Pink	The dimethyl compd. gives similar reactions but a blue color with $FeCl_3$ and H_2S
1,2,4, *m*-Tolylenediamine	Yellow	Nil	Nil	...	...	Reduces Fehling's soln. in cold
1,3,4, *m*-Tolylenediamine	Yellow	Violet	Claret color			
p-Aminophenol	Yellow	Nil	Violet			
p-Aminodiphenylamine	Faint yellow	Reddish violet	Brick-red	...	...	Violet with quinone
o-, *m*-, *p*-Toluidine	Greenish	Nil	...	Nil	Nil	
2,4-Diaminophenol	Yellow	Nil	...	Purple	Green-blue	
Methyl *p*-aminophenol	Nil	Nil	Green	Nil, pink later	Yellow, slowly	
Quinone	Slight yellow	Nil	...	Pale yellow with $HgSO_4$	Brownish	Reduces Fehling's soln. cold. Purple black with ammoniacal copper chloride, violet with *p*-aminodiphenylamine
Hydroquinone	Slight yellow	Nil	...	Nil	Yellow	
Pyrogallol	Slight yellow	Reddish turning greenish black	...	Yellowish		
Gallic acid	...	...	...	Bright red		

possible. The petroleum ether should be washed with dilute acid to extract any bases that may have dissolved in that solvent. The use of acetic acid simulates the action of perspiration, which in contact with the fur may be an agency in setting up the irritation.

C. AROMATIC NITRO COMPOUNDS

1. Nitrobenzene

One of the large industrial uses of nitrobenzene is in the manufacture of aniline. It is also used widely in the formulation of explosives and inks.

Nitrobenzene, $C_6H_5NO_2$, is a colorless to pale-yellow, oily liquid with an odor strongly resembling that of oil of bitter almonds. Nitrobenzene is known commercially as oil of mirbane. It has a specific gravity of 1.205 at 15/4° C.; melts at 6° C.; boils at 210–211° C.; has a refractive index of 1.5529 at 20° C.; and has a flash point of 89° C. It is volatile with steam and is only slightly soluble in water. It is freely soluble in alcohol, benzene, ether, and many oils.

a. Physiological Response

Nitrobenzene is a blood poison, causing the formation of methemoglobin. It can be absorbed by the body through the skin and in industrial plants this is a principal cause of nitrobenzene poisoning. Thus, spilling the compound on the clothes, or its presence in dyed shoes or in soap are all means of its entrance through the skin into the body.

The vapor is considered to be more toxic than the liquid and the inhalation of air containing comparatively large concentrations of nitrobenzene vapor may cause rapid physiological response. The principal symptoms are nausea, vomiting, unsteady gait, intoxication, coma, intense cyanosis, and respiratory failure. Nitrobenzene is not only a blood poison but it is also a nerve poison, for it paralyzes the central nervous system and thus causes tremors, muscular twitching, and other manifestations of nerve injury. Some of the nitrobenzene is excreted in the urine as *p*-aminophenol and some as the free poison. The maximum allowable concentration recommended for nitrobenzene is 1 part per million.

b. Detection and Determination

Nitrobenzene is detected and estimated by two main methods. It is trapped and then reduced to aniline and detected or estimated in terms of this compound, or it is further nitrated to *m*-dinitrobenzene and detected and estimated as that compound. The latter method is to be preferred.

Aniline Method. Trap the nitrobenzene vapor by bubbling air through an efficient bubbler containing water. Transfer the mixture to a flask and reduce the nitrobenzene by the addition of granulated zinc and hydrochloric acid. When there is no perceptible odor of nitrobenzene, filter the mixture and add an excess of potassium hydroxide solution to decompose the double chloride of aniline and zinc. Extract this mixture with several portions of ether. Combine the ether extracts, evaporate and perform the tests given for aniline on page 710 and sequence.

Dinitrobenzene Method. Trap the vapor as detailed in the section on benzene, using a sampling bottle with 2 ml. of nitrating acid, which converts the nitrobenzene to dinitrobenzene, after which the methods for the detection and determination of dinitrobenzene apply.

2. Dinitrobenzene

m-Dinitrobenzene is the simplest of the dinitrobenzenes to manufacture, hence it is the one most commonly used. It is employed in the manufacture of explosives. It forms yellowish crystals which melt at 89–90° C.; it boils at 300–303° C. and is volatile with steam. It is relatively insoluble in cold water but is somewhat soluble in boiling water. It is soluble in alcohol and freely soluble in benzene, chloroform, and ethyl acetate.

Most cases of poisoning from this substance occur in connection with its use in the manufacture of explosives. This substance can be absorbed by the body through the skin or by inhalation through the lungs. The physiological response of the body to this poison is similar to that of nitrobenzene.

The detection and estimation of *m*-dinitrobenzene has been fully discussed under the section relating to the detection and determination of benzene (page 527).

3. Mononitrotoluene

Mononitrotoluene, $NO_2C_6H_4CH_3$, or mono oil, is a yellow liquid boiling in the range 222–238° C. and having a density of about 1.16 at 20/4° C. Commercial mononitrotoluene consists of a mixture of three isomers. Approximately 60 per cent is the *ortho* isomer, boiling point 222.3° C., 38 per cent is the *para* isomer, melting at 51.9° C., and 2 per cent is the *meta* isomer. This material is used in the production of explosives.

The recommended maximum allowable concentration is 5 parts of mononitrotoluene per million parts of air.

Mononitrotoluene may be sampled by use of sampling bottles containing 2 ml. of nitrating acid. It may then be estimated by the titanous chloride titration method or colorimetrically.

4. *Dinitrotoluene*

Dinitrotoluene, $(NO_2)_2C_6H_3CH_3$, DNT, is prepared from mononitrotoluene and is a mixture of isomers melting at about 56° C. When *o*-mononitrotoluene is nitrated it yields both 2,4-dinitrotoluene melting at 70.5° C. and 2,6-dinitrotoluene melting at 61° C., while the *p*-mononitrotoluene yields only the 2,4-dinitro compound of nitration. A little of the 2,5 and 3,4 isomers are also present, for these are formed from the *meta* isomer.

Dinitrotoluene is considered to have the same order of toxicity as trinitrotoluene, hence the recommended maximum allowable concentration is 1.5 mg. per cubic meter.

This material may be collected by use of a midget impinger containing alcohol. Make the solution alkaline and heat on a hot-water bath for $^1/_2$ hour to allow the initial violet color to fade. Compare the residual yellow color with known standards.

Dinitrotoluene may also be sampled by use of diethylaminoethanol in fritted bubblers or in midget impingers. Dinitrotoluene gives no color with the alkylaminoethanol but on the addition of alkali, a deep blue-green color is produced which may be estimated.

5. *Trinitrotoluene*

Trinitrotoluene, $C_6H_2CH_3(NO_2)_3$, familiarly known as TNT, is used extensively as an explosive. It is a yellowish crystalline solid, which melts at 82° C. and explodes at about 240° C. It is soluble in water with difficulty. It has a characteristic bitter taste.

Trinitrotoluene is a systemic poison and also causes dermatitis. It can be absorbed by the body through the skin, the lungs, and the gastrointestinal tract. It causes the formation of methemoglobin, cyanosis of the cheeks and lips, and a blue line on the gums similar to the blue line on the gums formed by lead poisoning.[47] Jaundice and severe liver damage may occur. The hair and skin of trinitrotoluene workers become stained a characteristic yellowish-orange color. The maximum allowable concentration recommended for this substance is 1.5 mg. per cubic meter of air. The toxicity of this material was studied by von Oettingen.[47a]

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[47] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939).

The amount of contamination in an atmosphere attributable to trinitrotoluene dust or fumes may be determined by the use of the titanous chloride method, as detailed for the estimation of *m*-dinitrobenzene on page 531.

Collect trinitrotoluene dust in a midget impinger using slightly acidified alcohol as the collection medium. It is best to trap the vapor by use of a fritted bubbler. Make the solution alkaline and compare the color which develops with appropriate standards.

Trinitrotoluene may also be sampled by use of a midget impinger or bubbler containing diethylaminoethanol.[48] A deep violet color is produced which may be estimated colorimetrically or by use of a spectrophotometer at 400 mμ.

Place 10 ml. of diethylaminoethanol in a dry midget impinger and draw sufficient air through the device to give a distinct color to the solvent. Empty the contents of the impinger tube into a glass-stoppered bottle and then rinse twice with 5 to 10 ml. Prepare a series of standards containing 5, 10, and 20 micrograms per ml. by diluting a stock solution of 10 mg. of trinitrotoluene per 100 ml. of diethylaminoethanol and aged for 2 days. Read the concentration of trinitrotoluene from a standard curve.

Goldman[48a] indicates methods for the estimation of dinitrotoluene, trinitrotoluene, and tetryl in the presence of one another by procedures based on the colors these substances give with alkali and with diethylaminoethanol.

6. Tetryl

Tetryl, $(NO_2)_3C_6H_2N(NO_2)CH_3$, *N*-methyl-*N*, 2,4,6-tetranitroaniline, methylpicrylnitramine, 2,4,6-trinitrophenylmethylnitramine, is a yellow, explosive solid melting at 130° C. and having a density of 1.57. It is insoluble or only slightly soluble in most of the common organic solvents but is very soluble in benzene and acetone.

The recommended maximum allowable concentration for this compound is 1.5 mg. per cubic meter of air.

[47a] W. F. von Oettingen, D. D. Donahue, R. K. Snyder, and A. R. Monaco, *U. S. Pub. Health Service, Bull. 285* (1944).

[48] F. H. Goldman and D. E. Rushing, *J. Ind. Hyg. Toxicol., 25,* 164 (1943).

[48a] F. H. Goldman, *J. Ind. Hyg. Toxicol., 24,* 121 (1942).

Trap the air to be tested for tetryl by passage through a fritted bubbler containing sulfuric acid (1:100). Make the solution alkaline and compare the resultant pink color with standards. This color tends to fade rapidly because of hydrolysis of the tetryl with the formation of picric acid and methylamine.

Tetryl may also be estimated by its reaction with diethylaminoethanol.[48b] Tetryl gives a deep-red color with ethanolamines.[48a] Trap the tetryl using a midget impinger containing diethylaminoethanol and measure the transmittance at 420 mμ.

D. NITROPHENOLS

1. Dinitrophenol

Three isomers of dinitrophenol are commercially available but the α 2,4-dinitrophenol is the most important. It is an intermediate in the manufacture of explosives and dyes. It is also used as a wood preservative. It is a yellow to yellowish-brown crystalline solid which melts at 112–114° C. and has a specific gravity of 1.683. It sublimes when heated carefully and is volatile with steam. It is sparingly soluble in water, 0.5 g. being soluble in 100 ml. of water; it is easily soluble in alcohol and freely soluble in benzene and fixed alkali solutions.

Dinitrophenol and other nitrated phenols are skin irritants. Dinitrophenol has been used in the treatment of obesity and some "anti-fat" patent medicines also have used it as an ingredient. A number of deaths have been reported from its use for this purpose.

The symptoms of the toxic effects of this compound are high fever, abnormal sweating, fall of blood pressure and rapid pulse and dermatitis.[49][51] It is excreted in the urine as 2,4-aminonitrophenol.[52]

Detection and Determination

Dinitrophenol may be detected by diazotization with nitrite and coupling with β-naphthol to yield a violet or wine color. It can be estimated by the general bromide-bromate method as detailed on page 705, or by the following modification of this method.

Modified Koppeschaar Method.[53] Bromide-Bromate Reagent.—Dissolve 2.7835 g. of potassium bromate, $KBrO_3$, or its equivalent and 12 g. of potassium bromide, KBr, in water and dilute to 1 liter. This is a 0.1 *N* solution. Standardize against 0.1 *N* sodium thiosulfate solution.

[48b] F. H. Goldman and D. E. Rushing, *J. Ind. Hyg. Toxicol.*, *25*, 195 (1943).

[49] F. E. Poole and R. B. Haining, *J. Am. Med. Assoc.*, *102*, 1141 (1934).

[50] J. M. Strang and F. A. Evans, *J. Am. Med. Assoc.*, *104*, 1957 (1935).

[51] M. L. Tainter and D. A. Wood, *J. Am. Med. Assoc.*, *102*, 1147 (1934).

[52] L. Schwartz, *U. S. Pub. Health Service, Bull. 249* (1939).

[53] W. F. Kunke, *J. Assoc. Official Agr. Chem.*, *20*, 592 (1937).

Procedure. Transfer an adequate aliquot of the sample to a 500-ml. iodine flask (Fig. 120). It may be in the form of an alkaline solution. Dilute the solution to about 100 ml. Add 25 ml. of the 0.1 *N* bromide-bromate solution by means of a pipette and then 10 ml. of concentrated hydrochloric acid solution. Immediately stopper the flask and swirl vigorously for 1–3 minutes. Remove the stopper quickly and add 5 ml. of 20 per cent potassium iodide solution, 20 g. of potassium iodide dissolved in water and made to 100 ml., taking care to avoid loss of bromine. Immediately restopper the flask and shake thoroughly for 1 minute. Remove the stopper, rinse down the neck of the flask and the stopper with water, and titrate the solution with 0.1 *N* sodium thiosulfate solution, using 1 per cent starch solution as the indicator near the end of the titration.

One ml. of 0.1 *N* bromide-bromate solution is equivalent to 0.0092 g. of 2,4-dinitrophenol.

2. *Picric Acid*

Picric acid or trinitrophenol is well known for its use as an explosive, although in this field it has been largely replaced by other explosives. Some of the commercial names for explosives containing picric acid or picrates are Melinite D, consisting entirely of picric acid, Melinite, Lyddite and Shellite, in which picric acid is mixed with dinitrophenol. Picric acid is also used in the match and leather industries and in the manufacture of colored glass, electric batteries, and textile mordants.

Picric acid, $C_6H_2OH(NO_2)_3$, is a pale-yellow, crystalline solid which is practically odorless and which has an intense bitter taste. It has a specific gravity of 1.763, melts at 122–123° C., and explodes above 300° C. or if it is heated rapidly. It also explodes by percussion. About 1.25 g. dissolves in 100 ml. of water. It is readily soluble in alcohol, ether, chloroform and petroleum ether.

Picric acid will stain the skin and hair yellow and will cause dermatitis if permitted to remain on the skin for some time. Cases of dermatitis have been known to occur even from the use of medicinal ointments containing trinitrophenol. Industrially, many cases occur during the manufacture of explosives.[52,54,55]

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[54] A. Hamilton, *J. Am. Med. Assoc., 68,* 1447 (1917).
[55] M. Mayer, *U. S. Pub. Health Repts., 34,* 2371 (1919).

Some of the symptoms exhibited by picric acid poisoning are inflammation of the skin, resembling dermatitis due to poison ivy, accompanied by constitutional disturbances such as headache, loss of appetite, nose bleed, and fever. In other patients the symptoms are chiefly gastrointestinal, with headache. The inhalation of picric acid-bearing dust produces a bronchitis which is characterized by a hacking cough, the spitting of blood, and irritation of the throat.

Detection and Determination

Picric acid-bearing dust may be trapped by passage of the contaminated air through a bubbler containing dilute sodium hydroxide solution or by the use of alcohol.

The alkaline picrate solution may be acidified with sulfuric acid, extracted with ether and recovered from the ether layers by evaporation.

An aqueous solution of picric acid is colored an intense red by potassium cyanide or by ammonium sulfide solution, but the color must be developed by allowing the mixture to stand or by heating. These reactions are also given by trinitrocresol but much more readily. By using known standards and measured quantities of test solution, the concentration of picric acid in the test solutions may be ascertained colorimetrically.

Titanous Chloride Method.[56,57] Dilute solutions of picric acid may be titrated with an accuracy of at least 1 per cent by use of the following modification of the titanous chloride method. The solutions may be made as directed on page 531.

Procedure. Add 30 ml. of 20 per cent tertiary sodium citrate solution to the test solution and then add 0.25 g. of solid sodium bicarbonate to displace the air in the flask. Pass a stream of carbon dioxide or nitrogen through the titration flask after having the gas pass through a spiral-type wash bottle containing a mixture of 10 per cent titanous chloride solution and sodium citrate solution and then through another bubbler containing water. After 3 to 5 minutes agitation by the inert gas, add the standard titanous chloride solution slowly from a burette until the mixture appears to be a dark-violet color. At this point the titanous salt is only present in slight excess equivalent to 1–3 ml. of 0.1 N solution. Continue the passage of carbon dioxide gas for 2 minutes and then

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[56] I. M. Kolthoff and C. Robinson, *Rec. trav. chim., 45,* 169 (1926).

[57] I. M. Kolthoff and N. H. Furman, *Volumetric Analysis*, New York, 1929.

acidify with 20 ml. of concentrated hydrochloric acid. Add 5 ml. of 10 per cent potassium or ammonium thiocyanate solution to act as the indicator, and titrate the excess titanous chloride solution with standardized ferric sulfate solution until the pale red-brown color no longer fades, even after 2 minutes. The thiocyanate solution must be added after the addition of acid and toward the end of the titration, if possible, otherwise it will be reduced by the titanous chloride solution.

Gravimetric Determination.[58] Picric acid gives many insoluble compounds such as those with naphthalene, cinchonine, and acridine. These may be used for its gravimetric estimation if it is present in sufficient quantity.

Preferably, the picric acid may be precipitated by the use of nitron acetate (4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole acetate) in a boiling dilute solution acidified with sulfuric acid. Filter off the precipitate, dry at 105° C., cool, and weigh. The weight multiplied by 0.4232 yields the quantity of picric acid. The test solution must be free of chlorides, bromides, iodides, perchlorates, nitrates, and chromates.

E. OTHER AMINO AND NITRO COMPOUNDS[59,60]

Of lesser importance as industrial poisons may be mentioned *p*-nitroaniline, *m*-nitroaniline, the toluidines, *o*- and *p*-nitrophenol, and picramic acid (4,6-dinitro-2-aminophenol). These substances are used in the manufacture of dyes and other organic compounds and in the production of explosives. Some of them are used in the textile industry in dyeing. They are, in general, systemic poisons and cause dermatitis.

The dust and fumes of these substances may be sampled by methods previously detailed, the amino compounds in sulfuric acid solution and the phenols in solutions of the fixed alkalis. Those compounds that may be estimated with a fair degree of accuracy by the bromide-bromate method are listed in Table 30.

The titanous chloride method may be used to estimate *p*- and *m*-nitroaniline; *o*- and *p*-nitrophenol; *m*-nitro-*p*-toluidine; 1,2,4-dinitrotoluene; and picramic acid. Six equivalents of titanous chloride are required for the reduction of one nitro group, hence 1 ml. of 0.05 *N* titanous chloride is equivalent to 0.00011675 g. of nitrogen.

[58] Von M. Busch and G. Blume, *Z. angew. Chem.*, *21*, 354 (1908).

[59] A. R. Day and W. T. Taggart, *Ind. Eng. Chem.*, *20*, 545 (1928).

[60] F. L. English, *Ind. Eng. Chem.*, *12*, 994 (1920).

F. CHLORONITROBENZENES

1. *Chloronitrobenzene (Nitrochlorobenzene)*

The commercial product of chloronitrobenzene, or nitrochlorobenzene, is a mixture of the *o*- and *p*- isomers. It is a liquid known as Tropfoel and is used in the explosives industry as an intermediate. The *o*- and *p*-compounds in the pure state are solids.

This compound is a blood poison analogous to nitrobenzene. Ashcroft states that it causes poisoning by the pulmonary route, that it affects the blood, that its effect is cumulative, and that it is probably reduced in the body to chloroaniline, which is also poisonous.[61] Flury and Zernik[62] state that nitrochlorobenzene is more poisonous than nitrobenzene. The toxicity of this compound and related compounds has been compared by Mayer.[63]

2. *Chlorodinitrobenzene (Dinitrochlorobenzene)*

Dinitrochlorobenzene, $C_6H_3(NO_2)_2Cl$, chlorodinitrobenzene, is used in the coal tar dye industry, principally in the manufacture of sulfur blocks. It is a yellowish crystalline solid which melts at 52–54° C.; boils at 315° C.; and has a specific gravity of 1.7. It is insoluble in water, somewhat soluble in alcohol, and freely soluble in ether, benzene, and carbon disulfide.

Dinitrochlorobenzene dust has a similar but even stronger physiological action than nitrochlorobenzene.[62] It is also irritating to the mucous membranes and is a most powerful skin irritant.[64]

Determination

Dinitrochlorobenzene is estimated by hydrolyzing the compound with the formation of dinitrophenol and a chloride. The dinitrophenol formed is estimated colorimetrically.

Pass the air to be tested through an absorption vessel equipped with porous glass plates containing 10 ml. of alcohol. Transfer the alcoholic solution to a volumetric flask and rinse the absorption flask repeatedly with 1-ml. portions of alcohol. Make to volume with alcohol. Transfer 5 ml. of the test solution to a test tube and add 5 ml. of 10 per cent sodium hydroxide solution. Heat for 1 hour in a water bath at 40° C.

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[61] A. Renshaw and G. V. Ashcroft, *J. Ind. Hyg.*, *8*, 67 (1926).

[62] F. Flury and F. Zernik, *Schaedliche Gase*, Springer, Berlin, 1931.

[63] M. Mayer, *U. S. Pub. Health Repts.*, *34*, 2371 (1919).

[64] L. Schwartz, *U. S. Pub. Health Service, Bull. 215* (1934).

in order to hydrolyze off the chloride. When hydrolysis is complete, dilute to 10 ml. with water and compare colorimetrically with standards.[65]

Preparation of Standard. Prepare a solution containing 0.02 mg. of dinitrophenol per ml. in 10 per cent sodium hydroxide solution. Transfer suitable volumes of this stock solution to similar tubes and add sufficient 10 per cent sodium hydroxide solution to make 5 ml. Then add 5 ml. of alcohol. The usual standards contain from 0.001–0.01 mg. of dinitrophenol per ml.

G. NITROPARAFFINS

With the development of methods for the production of large quantities of nitroparaffins has come their utilization as solvents for vinyl resins, nitrocellulose, resins, dyes, oils, fats and waxes, and cellulose esters such as cellulose acetate, triacetate, and acetobutyrate. They are also useful in the synthesis of many organic compounds. The physical properties of some of these compounds are listed in Table 32.

1. Nitromethane

Nitromethane, CH_3NO_2, is a liquid of mild odor. It has a specific gravity of 1.139 at 20° C., a boiling point of 101.2° C., a flash point of 112° F. (Tag open cup), and a refractive index of 1.3818 at 20° C. About 9.5 ml. of this solvent is soluble in 100 ml. of water, while 2.2 ml. of water is soluble in 100 ml. of the solvent.

The physiological response of animals to the nitroparaffins was studied by Machle, Scott, and Treon.[66,67] Maximum allowable concentrations have been set for some of these compounds; thus for nitromethane it is 100 parts per million parts of air by volume.[68]

Determination

Nitromethane forms a color when heated with vanillin in ammoniacal solution. This reaction forms the basis of a method for its estimation.[69] However, since the color produced does not follow the Beer-Lambert law, it is necessary to run two standards, one having a lower concentration and the other having a higher concentration than the unknown.

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[65] B. A. Rashkovan, *Chimie et industrie, 36,* 308 (1936); *Chem. Abstracts, 30,* 7495, 8075 (1936).

[66] W. Machle, E. W. Scott, and J. Treon, *J. Ind. Hyg. Toxicol., 22,* 315 (1940); *24,* 5 (1942).

[67] W. Machle and E. Scott, *Proc. Soc. Exptl. Biol. Ind., 53,* 42 (1943).

[68] E. W. Scott, *J. Ind. Hyg. Toxicol., 24,* 226 (1942); *25,* 20 (1943).

[69] After W. Machle, E. W. Scott, and J. Freon, *J. Ind. Hyg. Toxicol., 22,* 315 (1940).

TABLE 32. Properties and Toxicity of Mononitroparaffins and Derivatives[69]

Compound	Formula	M. w.	Vapor pressure, mm. at 25° C.	Sp. gr. at 20/20° C.	Melting point, deg C.	Boiling point, deg C.	Sol. in 100 parts H_2O	Refractive index at 20° C.	Lethal dose (for rabbits by oral administration) in g./kg. lies between	Max. allowable concentration ppm.
Nitromethane	CH_3NO_2	61.0	38	1.139	−28.5	101	5.2	1.3818	0.75–1.00	100
Nitroethane	$C_2H_5NO_2$	75.1	25	1.052	−50	115	3.2	1.3916	0.50–0.75	100
1-Nitropropane	$C_3H_7NO_2$	89.1	13	1.003	....	131	1.3	1.4015	0.25–0.50	100
2-Nitropropane	$CH_3CH(NO_2)CH_3$	89.1	20	0.992	....	118	1.85	1.3944	0.50–0.75	50
1-Nitrobutane	$C_4H_9NO_2$	103.1	5	0.977[c]	....	151	0.5	1.4104	0.50–0.75	
2-Nitrobutane	$CH_3CH(NO_2)C_2H_5$	103.1	8	0.973[c]	....	139	0.9	1.4048	0.50–0.75	
Chloropicrin	Cl_3CNO_2	164.4	25	1.658	−69	112	....	1.460	....	
1-Chloro-1-nitroethane	$CH_3CHCl(NO_2)$	109.5	..	1.258	....	122–8.5	<0.4	1.423	0.10–0.15	
1-Chloro-1-nitropropane	$CH_3CH_2CH(NO_2)Cl$	123.5	..	1.209	....	139.5–143.3	<0.8	1.430	....	
2-Chloro-2-nitropropane	$CH_3CCl(NO_2)CH_3$	123.5	..	1.197	....	.....	....	....	0.50–0.75	
1,1-Dichloro-1-nitroethane	$CH_3C(NO_2)Cl_2$	144.0	..	1.405	....	122–5	<0.5	1.441	....	
1,1-Dichloro-1-nitropropane	$CH_3CH_2C(NO_2)Cl_2$	158.0	..	1.314	....	141–3.6	<0.5	1.443	....	
2-Nitro-1-butanol	$CH_3CH_2CH(NO_2)CH_2OH$	119.1	..	....	−47 to −48	105^{10}	20	....	....	
2-Nitro-2-methyl-1-propanol	$CH_3C(NO_2)(CH_3)CH_2OH$	119.1	..	....	90–1	94.5^{10}	350	....	1.00–2.00	
2-Nitro-2-methyl-1,3-propanediol	$CH_3C(NO_2)(CH_2OH)_2$	135.1	..	....	147–9	.....	80	....	1.00–2.00[a]	
2-Nitro-2-ethyl-1,3-propanediol	$(CH_2OH)_2C(NO_2)C_2H_5$	149.2	..	....	56–57	.....	400	....	....	
2-Nitro-2-methylol-1,3-propanediol (Tris(hydroxymethyl)nitro methane)	$NO_2C(CH_2OH)_3$	151.1	..	....	165–70	.....	220	....	0.25–0.50[b]	
2-Amino-1-butanol	$CH_3CH_2CH(NH_2)CH_2OH$	89.1	..	0.944	−2	178	∞	....	....	
2-Amino-2-methyl-1-propanol	$CH_3C(NH_2)(CH_3)CH_2OH$	89.1	..	0.934	30–31	165.5	∞	....	1.00–2.00	
2-Amino-2-methyl-1,3-propanediol	$CH_3C(NH_2)(CH_2OH)_2$	105.1	..	....	108–9	$151–2^{10}$	250	....	1.50–2.00	
2-Amino-2-ethyl-1,3-propanediol	$(CH_2OH)_2C(NH_2)C_2H_5$	119.2	..	1.099	37.5–8.5	$152–3^{10}$	∞	....	....	
2-Amino-2-methylol-1,3-propanediol (Tris(hydroxymethyl) nitro methane)	$NH_2C(CH_2OH)_3$	121.1	..	....	171–2	$219–20^{10}$	80	....	1.00–2.00	
2-Amino-2-methyl-1-propanol (neutralized solution)									1.00–2.00	
2-Amino-2-methyl-1,3-propanediol (neutralized solution)									Greater than 3.00	
2-Amino-2-methylol-1,3-propanediol (neutralized solution)									Greater than 5.00	

Sample the air by use of evacuated bulbs and absorb the nitroparaffin in 0.1 *N* sodium hydroxide solution. Carry out the determination on an aliquot of the sample. It is necessary to have an excess of alkali and it is preferable to make the analysis within 24 hours.

Procedure. Add 2 ml. of 2 per cent (by weight) ammonium hydroxide solution and 5 ml. of a 2 per cent solution of vanillin in methyl alcohol, prepared fresh as used, to an aliquot, containing from 0.1 to 0.3 mg. of nitromethane, in a Pyrex test tube. Make up the mixture to 10 ml. and heat for 30 minutes in a water bath at 60° C., with occasional shaking. Carry the standards and blank through the same operations as the unknown. Cool to room temperature and dilute to 25 ml. Read the densities of the sample and the standards against the blank at 500 mμ in 4-inch cells in a spectrophotometer. Plot the densities of the known solutions against their concentrations, and obtain the concentration of the unknown by interpolation.

2. *Nitroethane*

Nitroethane, $CH_3CH_2NO_2$, is a liquid. It has a specific gravity of 1.053, a boiling point of 114° C., a flash point at 106° F., and a refractive index of 1.3916. About 4.5 ml. of nitroethane is soluble in 100 ml. of water, while 0.9 ml. of water is soluble in 100 ml. of this nitroparaffin.

Its toxicity has been studied by the investigators[69] mentioned above. The recommended maximum allowable concentration is 100 parts of nitroethane per million parts of air by volume.

Determination

Primary mononitroparaffins, with the exception of nitromethane, react with ferric chloride in acid solution, pH 1.25 to 1.30, to form a pink color.[70] Nitroethane, 1-nitropropane, and 1-nitrobutane form stable colors but the color of the complexes formed with 2-nitropropane and 2-nitrobutane fades rapidly.

Obtain air samples by the use of evacuated bulbs and absorb the nitroparaffin in 0.1 *N* sodium hydroxide solution.

Procedure. Neutralize an aliquot of the sample containing from 1 to 20 mg. of nitroethane in 1 to 15 ml. of solution in a 25-ml. volumetric flask and treat with 1.5 ml. of 20 per cent sodium hydroxide solution. Allow to stand for 15 minutes, and acidify with 6 ml. of hydrochloric acid (1:7) to bring the mixture to the proper pH. Immediately add 0.5 ml. of 10 per cent ferric chloride solution. Treat a standard solution of the nitroparaffin of approximately the same concentration similarly. Allow to stand for 15 minutes and dilute to the mark. Compare in a colorimeter equipped with a 1.59-cm. (0.625-inch) Wratten filter No. 65A in B glass (Eastman Kodak Co.). When concentrations of less than 15 mg. of nitroethane are being estimated, it is best to reduce the amount of ferric chloride added to lessen the color interference.

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[70] E. W. Scott and J. F. Treon, *Ind. Eng. Chem., Anal. Ed., 12,* 189 (1940).

3. *Nitropropanes*

1-Nitropropane, $CH_3CH_2CH_2NO_2$, is also a liquid. Its specific gravity is 1.003, it boils at 131.6° C., it has a flash point at 120° F., and its refractive index is 1.4015. This solvent is less soluble in water, for 100 ml. of water will dissolve 1.4 ml. of 1-nitropropane. Conversely, 0.5 ml. of water is soluble in 100 ml. of 1-nitropropane.

2-Nitropropane, $CH_3CH(NO_2)CH_3$, is a liquid. It boils at 120.3° C., has a specific gravity of 0.992, a flash point at 103° F., and a refractive index of 1.3941. About 1.7 ml. of 2-nitropropane will dissolve in 100 ml. of water, while 0.6 ml. of water is soluble in 100 ml. of this nitroparaffin. The toxicity of nitropropanes has been studied by the investigators[69] mentioned above. A maximum allowable concentration of 50 parts per million has been recommended for 2-nitropropane. Silverman and coworkers[71] suggest, on the basis of sensory response, 100 parts of 1-nitropropane per million parts of air as the maximum allowable concentration for this compound.

The concentration in air of these nitroparaffins may be ascertained by use of the methods detailed above and by use of those in Chapter XII.

H. CHLORONITROPARAFFINS

1. *Chloropicrin*

Chloropicrin is an ill-chosen name for this compound, for it implies some resemblance to picric acid, which it does not resemble. It probably derived its name from its formation by Stenhouse in 1848 from the action of picric acid on calcium hypochlorite. It was known as Vomiting Gas to the British, Aquinite to the French, and Klop to the Germans. Its American symbol is PS.

Chloropicrin, trichloronitromethane, nitrochloroform, CCl_3NO_2, is a colorless, slightly oily liquid with a characteristic anise-like, sweet smell. It boils at 112° C. and has a specific gravity of 1.651 at 20°/4° C. Its density with respect to air is 5.7. It has a refractive index of 1.4607 at 23° C. It has a higher vapor pressure than water; at 10° C. this pressure equals 10.9 mm. of mercury, at 20° C., it is 16.9 mm., and at 30° C., it is 30.5 mm. About 0.14 g. of chloropicrin is soluble in water at 25° C. but it is soluble in all proportions in alcohol and ether.

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[71] L. Silverman, H. F. Schulte, and M. W. First, *J. Ind. Hyg. Toxicol.*, 28, 262 (1946).

Chemically, chloropicrin is a stable compound. It is not hydrolyzed nor affected by cold water nor by cold mineral acids. Aqueous sodium hydroxide has no effect on it but it is slowly decomposed by alcoholic sodium hydroxide. It is rapidly decomposed by sodium ethylate, alcoholic sodium cyanide and sodium sulfite, and heat.

a. Physiological Response

Chloropicrin is a toxic lung irritant and a strong lachrymatory agent. If it gets into the stomach it causes intense distress by producing nausea, vomiting, colic, and diarrhea. Chloropicrin has good warning properties and is used industrially as a warning agent in commercial fumigants. Chloropicrin is more toxic than chlorine but less lethal than phosgene. A concentration of 2.0 mg. per liter for an exposure of 10 minutes is lethal, as is a concentration of 0.8 mg. for an exposure of 30 minutes.[72]

b. Detection and Determination

Dimethylaniline Reaction. Preparation of Test Papers.—Soak strips of filter paper in a 5–10 per cent solution of dimethylaniline in benzene.

Expose the paper, which is white in color, to the atmosphere to be tested, or if the concentration of the contaminant is low, wave gently in the suspected atmosphere. The paper changes from white to yellow or maroon in the presence of chloropicrin. Chlorine, bromine, and nitrous gases also give a color with this reagent but of a different shade.

Carbylamine Reaction. Chloropicrin gives the Beilstein flame test for chlorinated hydrocarbons and because it has a trihalogenated carbon atom, it will give the carbylamine reaction. Pass the suspected gas into 2 ml. of hot alcoholic potassium hydroxide solution containing 1 drop of aniline and heat. The characteristic foul odor of phenylisocyanide results.

Sodium Sulfide Test. Add 1 drop of the material to 5 ml. of 20 per cent sodium sulfide solution. Close the tube. Shake. The typical pungent odor of chloropicrin immediately disappears.

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[72] A. M. Prentiss, *Chemicals in War,* McGraw-Hill, New York, 1937.

Nitrite Test. When chloropicrin is passed into a solution of sodium ethylate, it is decomposed with the formation of chloride and nitrite:[73]

$$CCl_3NO_2 + 4C_2H_5ONa \longrightarrow C(OC_2H_5)_4 + 3NaCl + NaNO_2$$

The presence of chloride can be demonstrated with silver nitrate and the Griess-Ilosvay reagent can be used to show the presence of nitrite.

Reagents. (a) Sulfanilic Acid Solution.—Dissolve 1 g. of sulfanilic acid in hot water, cool, and dilute to 100 ml.

(b) α-Naphthylamine Hydrochloride Solution.—Boil 0.5 g. of the salt with 100 ml. of water, kept at constant volume for 10 minutes. Decolorize with activated charcoal, if necessary.

If desired, a saturated solution of sulfanilamide may be used in place of (a) and a 0.1 per cent aqueous solution of N-(1-naphthyl) ethylenediamine dihydrochloride can be used in place of (b).

Aspirate the air to be tested through absolute alcohol. Add a small piece of 8 per cent sodium amalgam. After a few minutes decant the solution from the mercury. Acidify with acetic acid, adding the acid drop by drop, and then add 1–2 ml. of the Griess sulfanilic acid-α-naphthylamine reagent. After 10 minutes heat on a water bath. If much nitrous acid is present the red coloration will form even in the cold.

Chloropicrin can also be decomposed in this manner by passage through a methyl alcohol solution of potassium iodide, with the formation of chloride and nitrite:

$$CCl_3NO_2 + 4KI \longrightarrow CI_4 + 3KCl + KNO_2$$

Add a few drops of acetic acid to this solution, then the Griess reagent, and continue as above.

Diphenylamine Reaction. The presence of nitrite may also be shown by the diphenylamine reaction. Pass the air through a few drops of concentrated sulfuric acid. Add a few crystals of diphenylamine. A blue color develops if nitrites are present. To confirm, add a small crystal of ferrous sulfate. A brown color indicates oxides of nitrogen. Chlorine, stannic chloride, and titanium chloride produce a blue color also but do not give the confirmatory test.

Nitroso Reaction. If sufficient of the sample is obtainable, a drop of the suspected sample is boiled with a 5 per cent alcoholic potassium hydroxide solution, or the suspected air is passed through the hot solution and a few crystals of resorcinol are added. A red color due to the formation of a nitroso compound is obtained on the addition of sulfuric acid. With thymol a yellow color is produced without the addition of acid.

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[73] H. Hennig, *Gasschutz u. Luftschutz*, 7, 18 (1937); *Chem. Abstracts*, *31*, 2311 (1937).

Combustion Methods. Chloropicrin can be detected by combustion methods. If an atmosphere containing the gas is passed through a quartz tube heated to 450° C., the chloropicrin contaminant will decompose with the formation of chlorine. This can be detected by bubbling through a potassium iodide solution containing starch solution as indicator. The liberated iodine will color the starch blue.

2. 1,1-Dichloro-1-nitroethane

1,1-Dichloro-1-nitroethane is used as a fumigant. Its specific gravity at 20° C. is 1.405; it boils in the range of 122–125° C.; it has a flash point of 168° F.; and it has a refractive index of 1.441 at 20° C. Less than 0.5 ml. of this chloronitroparaffin is soluble in 100 ml. of water at 20° C. but it is miscible with most organic solvents.

1,1-Dichloro-1-nitroethane is a lung and skin irritant producing pulmonary edema in high concentrations. In a study[74] it was found that the lethal oral dose for rabbits is between 0.15 and 0.20 g. per kilo and that exposure to concentrations in excess of 52 parts per million (0.3 mg. per liter) for longer than 1 hour was dangerous. Concentrations of half that amount did not kill animals exposed for 204 hours. The recommended maximum allowable concentration is 10 parts of 1,1-dichloro-1-nitroethane per million parts of air.

Determination

1,1-Dichloro-1-nitroethane reacts, as does chloropicrin, with resorcinol and alkali to give a colored compound. This reaction is used as a basis for its colorimetric determination.

Sample the atmosphere by use of evacuated flasks or trap the air using an impinger containing methyl alcohol. Subsequently add methyl alcohol to the evacuated sample bottle and shake to absorb the chloronitroparaffin.

Procedure. Transfer with the aid of a pipette an aliquot of 6 ml. or less containing not more than 0.9 mg. of the chloronitroparaffin to a 25-ml. volumetric flask and if the volume is not 6 ml., make up to 6 ml. with methyl alcohol. Cool in a refrigerator for 30–60 minutes. Add 1 ml. of a 5 per cent solution of resorcinol in methyl alcohol and 2 ml. of a 5 per cent aqueous sodium hydroxide solution. Add water to make the volume total 23 ml. and then allow the mixture to stand in a refrigerator for 4 hours for the development of a green color. Add 2 ml. of *N* sulfuric acid to change the color to light tan and read against a water blank in 1-inch matched cells in a photoelectric spectrophotometer at 480 mμ. Deduct the blank and obtain the concentration from a previously prepared standard curve.

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[74] W. Machle, E. W. Scott, J. F. Treon, F. F. Heyroth, and K. V. Kitzmiller, *J. Ind. Hyg. Toxicol.*, *27*, 95 (1945).

The color is stable for 18 hours in a refrigerator. The standard curve should be checked repeatedly and a new curve should be prepared for a new lot of methyl alcohol. The reagents should be kept in a refrigerator.

3. 1-Chloro-1-nitropropane

1-Chloro-1-nitropropane is a chloronitroparaffin which has been suggested as an antigelling agent for rubber cements containing high accelerators and as a solvent for fats and waxes. 1-Chloro-1-nitropropane has a specific gravity of 1.209 at 20° C.; 90 per cent boils in the range 139.5–143.3° C.; it has a flash point of 144° F.; and its refractive index at 20° C. is 1.430. Less than 0.8 ml. of this chloronitroparaffin is soluble in 100 ml. of water at 20° C. and conversely less than 0.4 ml. of water is soluble in 100 ml. of this compound.

1-Chloro-1-nitropropane is a lung irritant and high concentrations may induce pulmonary edema but in contradistinction to 1,1-dichloro-1-nitroethane, it is not a skin irritant and its vapor is somewhat less toxic.[74] The recommended maximum allowable concentration is 20 parts of 1-chloro-1-nitropropane per million parts of air by volume.

Determination

1-Chloro-1-nitropropane reacts with phenylhydrazine in concentrated sulfuric acid to produce a red color, hence it may be estimated by use of this reaction.

Procedure. Place a 1-ml. aliquot of the sample in absolute alcohol, obtained as in the preceding section by shaking a sample obtained by use of an evacuated bottle with absolute alcohol, into a 10-ml. glass-stoppered graduated cylinder. The aliquot should not contain more than 0.6 mg. of 1-chloro-1-nitropropane. Add 1 ml. of a phenylhydrazine reagent prepared by diluting 1 ml. of a 2 per cent solution of phenylhydrazine in 50 per cent aqueous alcohol to 10 ml. with concentrated sulfuric acid. Shake, cool in ice, add 4 ml. of concentrated sulfuric acid, shake again, and heat in a water bath at 100° C. for 1 hour with occasional shaking. Remove from the bath, cool, dilute to 10 ml. with sulfuric acid (6:4), and read in a photoelectric spectrophotometer at 540 mμ using 10-mm. matched glass cells.

The amount of 1-chloro-1-nitropropane may be estimated from the density by two methods: (1) Prepare two standards containing 0.10 and 0.60 mg. of the chloronitroparaffin using them along with the samples; calculate the amount in each sample by interpolation of their densities and the densities of the standards. (2) Prepare a standard curve by determining the average densities of four samples of each of four standard solutions containing various quantities of 1-chloro-1-nitropropane.

I. NITRATE ESTERS

1. Ethylene Glycol Dinitrate

Glycol dinitrate is widely used in the manufacture of explosives. Ethylene glycol dinitrate, $C_2H_4(ONO_2)_2$, is a yellow liquid which boils at 114–116° C. with explosion. It has a density of 1.483. It is insoluble in water but is soluble in alcohol. It is decomposed by alkalies.

Glycol dinitrate produces toxic effects. It may be absorbed through the skin or by inhalation, causing vasodilation resulting in a fall of blood pressure, tachycardia, and headache. The symptoms are similar to those produced by nitroglycerin and are probably attributable to the nitrate rather than to the glycol. Since it is more volatile than nitroglycerin, its vapors have a stronger physiological action. The effects of ethylene glycol dinitrate and mononitrate have been reviewed by von Oettingen.[75]

The phenoldisulfonic acid reaction adapted by Scoville[76] for nitroglycerin may be used for ethylene glycol dinitrate[77] when modified by using acetone instead of alcohol as the solvent.

Sampling. Pass a known volume of the air containing ethylene glycol dinitrate through two U-tubes immersed in acetone-solid carbon dioxide freezing mixtures. The dinitrate is condensed and collects almost entirely in the first U-tube.

Procedure. Wash the tubes carefully with acetone, after transferring the contents to a volumetric flask, and make up to volume with that solvent. Transfer an accurate aliquot between 1 and 5 ml. of this acetone solution, according to the concentration of the dinitrate, to a 50-ml. porcelain dish and allow the acetone to evaporate spontaneously. Treat the residue of ethylene glycol dinitrate with 2 ml. of phenoldisulfonic acid solution (page 354) and stir the mixture thoroughly with a glass rod. Let stand for about 10 minutes, dilute the contents with water, and transfer to a 100-ml. volumetric flask. Wash the dish and add the washings to the flask. Make the acid solution alkaline with ammonium hydroxide solution (1:1). After cooling to room temperature, dilute to 100 ml. with water and compare with standards. The yellow solution may also be transferred to a 10-ml. observation tube for examination in a spectrophotometer. Observations are best made at 4900 Å.

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[75] W. F. von Oettingen, *U. S. Pub. Health Service, Nat. Inst. Health Bull. 186* (1946).

[76] W. L. Scoville, *Am. J. Pharm., 83,* 359 (1911).

[77] J. H. Foulger, *J. Ind. Hyg. Toxicol., 18,* 126 (1936).

The concentration of this nitrate ester in air may also be obtained by use of the xylenol method detailed below.

2. Nitroglycerin

Nitroglycerin is used principally as an explosive or as a component of explosives. It is also used medicinally. Nitroglycerin, glycerol trinitrate, trinitrin, $C_3H_5(ONO_2)_3$ is a yellow liquid which boils at 260° C. with explosion. Its specific gravity is 1.60. It has an appreciable vapor pressure, being about as volatile as mercury. It is somewhat soluble in water, very soluble in alcohol, and is miscible with ether.

Nitroglycerin is a strong vasodilator. Symptoms of nitroglycerin poisoning are pounding of the heart, flushing of the face, throbbing in the head, and intense headache. Nervous disturbances, nausea, vomiting, and fainting may occur. A thorough review of the effects of glycerol trinitrate is given by von Oettingen.[75] Because of its marked physiological effect the maximum allowable concentration for this compound has been set at 0.5 part per million of air.

Determination

The concentration of nitroglycerin vapors in air may be ascertained by trapping the vapors in alcohol, evaporating the alcohol solution spontaneously, treating with phenoldisulfonic acid solution (page 354), making slightly alkaline with potassium hydroxide solution, and then comparing in a colorimeter against a standard solution of potassium nitrate.[76] The method of Foulger[77] (described on page 739) may be used, as may the following method.

Dilute the nitroglycerin test solution with alcohol and to 20 ml. of this solution add 1 ml. of potassium hydroxide solution, 15 g. of KOH in 100 ml. of solution. Allow the mixture to stand for 1$^1/_2$ hours. Evaporate the alcohol on a water bath, dissolve the residue in water, filter into a 50-ml. volumetric flask, and dilute to the mark with the washings and water. Use 20 ml. of this solution for the determination of nitrate and 5 ml. for the estimation of nitrite.

To determine the nitrate nitrogen evaporate the 20-ml. aliquot almost to dryness, adding to the residue 2 ml. of phenoldisulfonic acid reagent (page 354), the mixture being agitated and diluted to 100 ml. with water containing 20 ml. of 6 *N* ammonium hydroxide solution. Estimate colorimetrically with a standard solution, 1 ml. of which contains 4 μg. KNO_3.

Transfer the 5 ml. to be used for the nitrite determination to a 100-ml. volumetric flask, dilute with water to 60–70 ml., add 1 ml. 10 per cent tartaric acid solution (10 g. tartaric acid in 100 ml. of solution), and 10 ml. of the Greiss reagent (page 355). Allow to stand for 1 hour and compare colorimetrically with a standard solution containing 0.4697 micrograms of sodium nitrite in 1 ml.

Nitroglycerin can be estimated by this method in concentrations ranging from 0.005 to 10 mg. per liter of air.[78]

In the saponification of the nitroglycerin solution, 1 ml. of a 15 per cent solution of potassium hydroxide yields 1.662 mols of nitrite per mol of nitroglycerin, if the saponification is carried out for $1^1/_2$ hours, and 1.932 mols after 18–20 hours.[78]

In order to avoid the formation of by-products such as nitrites and cyanides which may be formed in the hydrolysis of nitroglycerin Goldman[79] recommends the following procedure.

Collect the nitroglycerin in a bubbler or midget impinger using ethyl alcohol as the collection medium and sampling at the customary rates. Evaporate the alcoholic nitroglycerin solution rapidly in a current of air and warm slightly to insure dryness. Add the phenoldisulfonic acid reagent (page 354) directly to the residue and proceed in the usual way to determine oxides of nitrogen.

A fritted bubbler containing triethylene glycol may also be used as the collection device. The nitroglycerin may then be estimated by the xylenol method.

Xylenol Method.[80] In this method, nitroglycerin or nitrate esters in general are hydrolyzed and the nitric acid formed is used for the simultaneous nitration of *m*-xylenol. The 4-hydroxy-1,3-dimethyl-5-nitrobenzene formed is separated from the reaction mixture by distillation after making it alkaline and the amount formed is estimated colorimetrically, by an evaluation of the deep-yellow color produced, which obeys the Beer-Lambert law.

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[78] N. P. Komar, P. E. Lyubimov, and V. A. Minakov, *J. Applied Chem. U.S.S.R.*, *7*, 429 (1934); *Chem. Abstracts*, *29*, 1748 (1935).

[79] F. H. Goldman, *J. Ind. Hyg. Toxicol.*, *24*, 121 (1942).

[80] H. Yagoda and F. H. Goldman, *J. Ind. Hyg. Toxicol.*, *25*, 440 (1943).

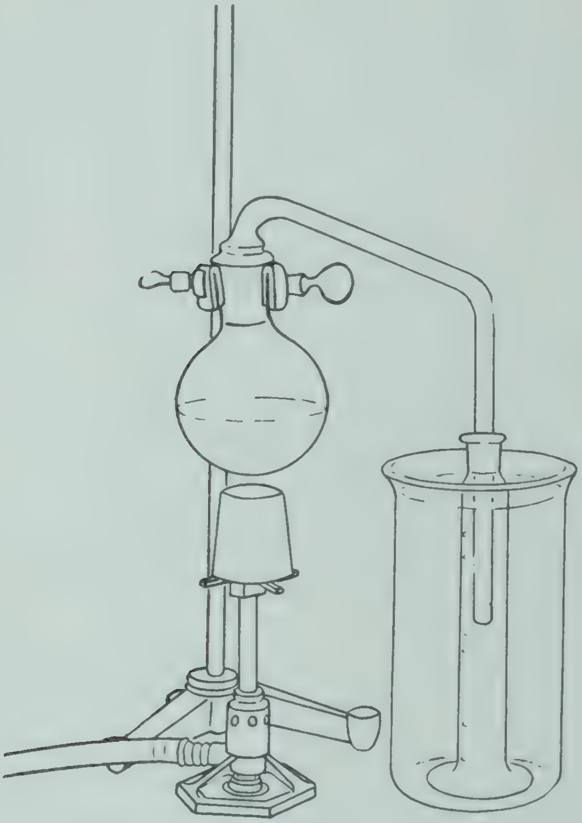


Fig. 121. Distillation apparatus for the *m-xylenol* method.

Sampling. Draw air through a midget impinger containing 10 ml. of triethylene glycol or propylene glycol at a rate of 3 liters per minute, and because of the low concentrations generally encountered, sample at least 60 liters, that is, continue sampling for 20 minutes. When many samples are collected in the field, each sample should be transferred to a small glass-stoppered bottle and the volume in the impinger should be recorded. This practice avoids dilution of the sample with rinse water.

Procedure. Transfer a 5-ml. aliquot to a 250-ml. standard taper flask and dilute with an equal volume of water. Add 0.1 ml. of 1 per cent *m*-xylenol dissolved in either triethylene or propylene glycol, which is adequate for 500 micrograms of nitroglycerin, stopper, and cool under running water. Add 17 ml. of concentrated sulfuric acid dropwise with constant cooling so that the temperature does not exceed 35° C. Allow to stand for 10 minutes. Dilute the mixture by the addition of 150 ml. of cold water, add a few chips of porcelain, and connect the flask to the distillation apparatus (Fig. 121).

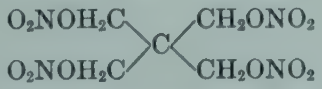
Bring the solution to the boiling point and reduce the size of the flame to about 2 cm. so that the distillate comes over at a rate of about 1 ml. per minute. Collect the distillate in a water-cooled 25-ml. graduated cylinder containing 1 ml. of 2 per cent sodium hydroxide solution. The bulk of the nitroxylenol should come over in the first few drops of distillate. Quantitative separation is achieved by stopping the distillation when the condensate reaches the 10-ml. mark on the cylinder. Mix the contents of the receiver and set aside for comparison.

Prepare a blank by distilling a system consisting of 5 ml. of the glycol used, 5 ml. of water, 0.1 ml. of 1 per cent *m*-xylenol in the glycol, and 17 ml. of concentrated sulfuric acid, following the identical procedure used for the unknown. Prepare a standard by substituting 5 ml. of 0.002 per cent potassium nitrate, containing 100 micrograms of KNO_3, for the 5 ml. of water used in the blank, add the other reagents, and proceed with the method. When the sample and the standard are of similar intensities, the concentration of the unknown can be evaluated by a comparison of the solutions with the aid of a Duboscq-type colorimeter. When the concentration falls below 50 micrograms of potassium nitrate, compare the unknown with a series of dilute standards prepared by distilling 10, 20, 30, and 40 micrograms of potassium nitrate.

Calculate the nitroglycerin content of the aliquot used by multiplying the matching quantity of potassium nitrate by 0.7486.

3. Pentaerythritol Tetranitrate

Pentaerythritol tetranitrate:



commonly known as PETN and other synonyms such as Penthrite and Hasethrol, is a nitric acid ester of the tetrahydric alcohol pentaerythritol. This ester is a powerful explosive and is used in detonating fuses. It has a specific gravity of 1.67 and melts at 140° C. Compared with other aliphatic nitric acid esters, pentaerythritol tetranitrate manifests little toxicity.[81]

It may be sampled and estimated in a manner analogous to that described for nitroglycerin. It may also be trapped in a fritted bubbler with triethylene glycol as the collection medium with subsequent colorimetric estimation by the xylenol method (page 741).

J. HETEROCYCLIC COMPOUNDS

1. Pyridine

Pyridine, C_6H_5N, is used industrially in the chemical industry; it is also used as a solvent for anhydrous mineral salts and as a denaturant for alcohol. It is a colorless liquid with a characteristic, disagreeable odor. It boils at 115–116° C.; has a specific gravity of 0.9780 at 25/4° C.; and a refractive index of 1.509 at 20° C. It is miscible with water, alcohol, ether, petroleum ether, and many organic liquids, but it is insoluble in aqueous alkali solutions.

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[81] W. F. von Oettingen, D. D. Donahue, A. H. Lawton, A. R. Monaco, H. Yagoda, and P. J. Valaer, *U. S. Pub. Health Service, Bull. 282* (1944).

a. Physiological Response

Pyridine exerts a local irritation on the mucous membranes and a general narcotic action on the central nervous system. Symptoms following exposure are irritation of the respiratory tract and of the eyes, cough, and, if in contact with the skin, dermatitis. The ingestion of pyridine will cause headache, vertigo, trembling of the extremities, and somnolence.

b. Determination

The concentration of pyridine in an atmosphere can most simply be estimated by drawing a measured volume of the contaminated air through an efficient bubbler containing a known volume of 0.1 *N* sulfuric acid. The excess sulfuric acid is determined by back-titration with standard alkali.

If small amounts of ammonia are also present, the pyridine content can be estimated by first precipitating the ammonia as NH_2HgCl and after filtering off the precipitate, titrating the remaining pyridine with standard 0.1 *N* acid, using methyl orange as the indicator.

Pyridine forms pyridine chloraurate, $C_5H_5NHAuCl_2$, and pyridine chloroplatinate, $(C_5H_5NH)_2PtCl_6$, which are slightly soluble in water. By means of the formation of these salts, pyridine may be estimated gravimetrically.

Thionyl Chloride Method. By heating pyridine with thionyl chloride, $SOCl_2$, 4-pyridylpyridinium dichloride is formed which on treatment with alkali gives glutaconic aldehyde, OHCCH:CHCH:CHONa, and 4-aminopyridine. Glutaconic aldehyde reacts in acid solution with aromatic primary amines to form colored Schiff's bases.

Procedure. Trap the pyridine in the air by methods previously detailed. Add a few drops of thionyl chloride to 1 drop of test solution. The thionyl chloride will react with any excess water in the test solution. Evaporate the mixture almost to dryness. Add a drop of water, a drop of 4 *N* sodium hydroxide solution, and then acidify with a few drops of a 1 per cent solution of α-naphthylamine in 2 *N* hydrochloric acid. Five micrograms of pyridine can be detected in a concentration limit of 1:10,000.

2. *Nicotine*

Industrial poisoning from nicotine occurs from two principal sources; these are its occurrence in tobacco and tobacco dust and its use as an insecticide. Most often such poisonings are a result of absorption through the skin, although in the case of tobacco dust, inhalation is a principal portal of entry. Pure nicotine is a colorless oil which boils at 247° C., has a density of 1.009 at 20/4° C., and has a refractive index of 1.5239 at 22.4° C. It is soluble in water, miscible with alcohol and ether, and very soluble in most common organic solvents.

Determination

Nicotine develops a color by reaction with cyanogen bromide and an aromatic amine in the presence of acetates. This reaction is used by Markwood[82] as the basis for a method for its estimation in tobacco leaf and by McCormick and Smith[83] for its estimation in air in the form of tobacco dust or vapor.

Reagents. To reduce the increase in temperature which results upon mixing the alcoholic reagents with water, to minimize temperature variations, and to obtain uniform results, it is best to keep the reagents in a refrigerator at 5° C.

Alcoholic Cyanogen Bromide Solution.—Because this reagent is toxic and irritating the manipulations of weighing and transferring in the preparation of this reagent should be performed under a hood. Cool reagent-grade cyanogen bromide, weigh out 6 g., dissolve in 95 per cent redistilled ethyl alcohol, and make up to 100 ml. with this solvent. Keep the solution in a dark bottle in the cold.

Alcoholic β-Naphthylamine Solution.—Dissolve 0.6 g. of reagent-grade β-naphthylamine in 95 per cent redistilled ethyl alcohol and make up to 100 ml. with this solvent. Keep the reagent solution in a dark bottle in the cold.

Alcoholic Potassium Acetate Solution.—Dissolve 2 g. of potassium acetate in 95 per cent redistilled ethyl alcohol and make up to 100 ml. with the same solvent.

Water of Adjusted pH.—Adjust distilled water just to the disappearance of color of phenolphthalein indicator by use of standard potassium hydroxide and acetic acid solutions.

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[82] L. N. Markwood, *J. Assoc. Official Agr. Chem., 22,* 427 (1939); *23,* 792 (1940); *23,* 804 (1940); *26,* 280 (1943).

[83] W. E. McCormick and M. Smith, *Ind. Eng. Chem., Anal. Ed., 18,* 508 (1946).

Standard Nicotine Solution.—Weigh accurately 20 to 25 mg. of reagent-grade nicotine in a small thin-walled glass bulb and seal. Break under water in a 50-ml. glass-stoppered flask, using a volume of water which is equivalent in ml. to the weight of nicotine in mg. This will give a solution in which 1 ml. contains 1 mg. of nicotine. Add the water from a burette, using the last drops for rinsing the stirring rod used to break the thin-walled bulb. Transfer 10 ml. of this solution to a 500-ml. volumetric flask and make to volume with water. This solution contains 20 micrograms of nicotine per ml. It is stable in the dark for at least 2 months.

Procedure. Add sufficient water to an all-glass impinger (page 137) to reach the 100-ml. mark. Draw the air to be sampled through the impinger at a rate of 1 cubic foot per minute. Continue sampling until about 50 micrograms have been collected. If kept in the dark such samples will have no appreciable diminution in nicotine content over a period of several days.

Adjust the volume of water in the impinger to 100 ml. Shake thoroughly and transfer a noted 10- to 11-ml. aliquot to a graduated 15-ml. centrifuge tube. Add 0.1 ml. of 30 per cent sodium hydroxide solution, stopper the tube, and shake at intervals during a 10- to 15-minute period. The alkali is used to liberate free nicotine from tobacco dust, hence if the vapor is being estimated this step may be omitted. At the end of the 15-minute period, whether or not alkali has been added, add 2 drops of phenolphthalein indicator solution and carefully neutralize with acetic acid, approaching the end point with acetic acid (1:20) and completing the titration with acetic acid (1:2,000), adding the latter solution with a microburette. Avoid an excess of acid. Read the volume to the nearest 0.1 ml. Centrifuge for at least 20 minutes at approximately 3000 r. p. m. If the dust is not completely deposited, replace the tube in the centrifuge and repeat centrifuging.

Transfer, with the aid of a pipette, 10 ml. of test solution to a colorimeter tube. Add 2 ml. of alcoholic potassium acetate solution and 4 ml. of alcoholic β-naphthylamine solution. Mix thoroughly and measure the transmission to obtain the amount of color attributable to the tobacco. Add 1 ml. of alcoholic cyanogen bromide solution, mix thoroughly, and place in the dark for 30 minutes at 22–28° C. for color development. Measure the light transmission with a photoelectric colorimeter or spectrophotometer at 490 mμ. Obtain the amount of nicotine present in the aliquot by reference to a calibration chart previously prepared by treating known amounts of nicotine by the method detailed. Use a blank tube, containing 10 ml. of distilled water and the same volume of all the reagents used for the unknown, to obtain the 100 per cent transmission reading.

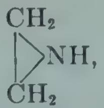
Calculate the total amount of nicotine in the impinger sample from the formula

$$\gamma_t = \frac{10\,\gamma\,V_2}{V_1}$$

where
γ_t = micrograms of nicotine in impinger
γ = micrograms of nicotine in 10-ml. aliquot as read from calibration chart
V_1 = volume in ml. of aliquot transferred from impinger for analysis
V_2 = volume in ml. after final neutralization

To prepare the calibration curve, transfer 0.25, 0.5, 1.0, and 2.0 ml. of the standard nicotine solution to colorimeter tubes. These volumes will contain respectively 5, 10, 20, and 40 micrograms of nicotine. Add sufficient water adjusted in pH to make the volume 10 ml. and then continue with the method as described. Plot transmission readings on the logarithmic axis against nicotine content in micrograms on the arithmetic axis of semilogarithmic graph paper.

3. *Ethylenimine*

Ethylenimine,  $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!>\!NH$, aziridine, also known by the names of ethylene imine, azirane, dihydroazirane, aminoethylene, and dimethyleneimine, is a colorless, oily liquid with a strong ammoniacal odor. It has a specific gravity of 0.832. It boils at 55–56° C. and has a vapor pressure of 160 mm. at 20° C.

Ethylenimine has found some industrial use and undoubtedly its use will increase in volume. This substance is poisonous and has an added hazard in that its odor resembles that of ammonia so closely that it fails to have warning power. Its toxicity has been studied by various investigators.[84,85] Ethylenimine is about twice to four times as toxic as ammonia. It is a skin sensitizer and necrotizing agent and in fluid form it

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[84] C. P. Carpenter, H. F. Smyth, Jr., and C. B. Shaffer, *J. Ind. Hyg. Toxicol.*, *30*, 2, 1948.

[85] S. D. Silver and F. P. McGrath, *J. Ind. Hyg. Toxicol.*, *30*, 7, 1948.

penetrates the skin readily but its vapors are not readily absorbed through the skin.

The concentration of ethylenimine in air can be estimated in a manner analogous to that used for ammonia. Draw air at a rate of 1 liter per minute through adequate bubblers containing known volumes of 0.1 *N* sulfuric acid. Titrate the solution with 0.1 *N* sodium hydroxide solution using a mixed indicator prepared by dissolving 0.04 g. of methyl red and 0.06 g. bromocresol green in 100 ml. of 95 per cent alcohol, and adding to this solution 1 ml. of 0.1 *N* sodium hydroxide solution.

Calculate the concentration of ethylenimine by evaluating the standard acid in terms of the material used at the plant.

Ethylenimine can be differentiated from ammonia by the formation of various organic derivatives.

K. ALIPHATIC AMINO COMPOUNDS

The aliphatic amines are used for various purposes, principally as intermediates for the manufacture of dyes, drugs, emulsifying agents, and other synthetic organic compounds, as solvents, in tanning, and for other uses. Methylamine is a gas. Ethylamine is a low boiling liquid. Most of the other common aliphatic amines are colorless liquids. They all have strong ammoniacal odors.

Since the aliphatic amines are alkaline, they irritate the upper respiratory system markedly and have an effect on the lungs. Their toxicity generally increases with increase in length of chain and the aliphatic diamines are more toxic than the monoamines.[86]

Determination

Since the aliphatic amines contain nitrogen in a suitable form, they may readily be estimated by variations of the micro-Kjeldahl method. In such methods as in macrodeterminations protein and other forms of nitrogen are converted to ammonia and are fixed as ammonium sulfate by digestion with sulfuric acid. The ammonia is liberated by the addition of sodium hydroxide solution, is distilled, trapped in standard hydrochloric acid, and the excess hydrochloric acid is estimated titrimetrically with standard sodium hydroxide solution. The apparatus used is that of Parnas and Wagner.[87] The variation is that of the authors.

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[86] J. H. Sterner in F. A. Patty, *Industrial Hygiene and Toxicology*, Vol. II, Interscience, New York, 1949.

[87] J. K. Parnas and R. Wagner, *Biochem. Z.*, *125*, 253 (1921).

Dilute an aliquot portion of the material being analyzed if necessary, to a known volume in a volumetric flask, so that the amount of protein nitrogen will be 0.1 or 0.2 mg. per ml. Transfer 1 ml. to a micro-Kjeldahl digestion flask. Add 1 ml. of concentrated sulfuric acid, 1 ml. of a 4 per cent copper sulfate solution to act as the catalyst, and 0.7 g. of potassium sulfate and digest on a digestion oven. Raise the heat slowly, boil vigorously, and after the material has been digested, as evidenced by a clear, straw yellow or light green color, reduce and cut off the heat. This process generally takes about 20 minutes. If the mixture does not clear in this time, reduce the heat, carefully add 2–3 drops of 30 per cent hydrogen peroxide and then continue heating for 5–10 minutes. Allow to cool, add 4 ml. of water, and stir to dissolve the salts.

Add 7.0 ml. of 0.01 *N* hydrochloric acid, accurately measured to a 25-ml. flask and add a trace of methyl red indicator solution. Allow the water in the steam generator to boil gently and open the pinch clamp or stopcock at the bottom of the steam trap so that the steam can escape. Transfer the digest from the micro-Kjeldahl digestion flask to the distillation tube through the small funnel. Wash out the micro-Kjeldahl digestion flask with two 2-ml. portions of water and add these washings to the distillation tube. Place the receiving flask under the condenser so that the tip of the silver tube condenser is below the standard acid. Add with the aid of a pipette 7 ml. of 30 per cent sodium hydroxide solution to the mixture in the distillation tube through the small funnel.

Close the stopcock or pinch clamp of the small funnel and on the steam trap thus compelling the steam to pass through the distillation tube. Distill for exactly 3 minutes. Lower the receiving flask so that the tip of the condenser is about 1 cm. above the surface of the distillate. Continue the distillation for another minute. Rinse the tip of the condenser tube with a few drops of water. Add another trace of methyl red indicator solution, if this is necessary. Titrate with standard 0.01 *N* sodium hydroxide solution. One ml. of standard hydrochloric acid is equivalent to 0.14 mg. of nitrogen. Run a blank and subtract the blank from the volume of standard hydrochloric acid.

Selected References

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Appendix

TABLE 1

Conversion Table for Gases and Vapors[1]

(Milligrams per liter to parts per million and vice versa, at 25° C. and 760 mm. of mercury barometric pressure)

Molecular weight	1 mg./l. ppm.	1 ppm. mg./l.	Molecular weight	1 mg./l. ppm.	1 ppm. mg./l.	Molecular weight	1 mg./l. ppm.	1 ppm. mg./l.
1	24,450	0.0000409	51	479	0.002086	101	242.1	0.00413
2	12,230	0.0000818	52	470	0.002127	102	239.7	0.00417
3	8,150	0.0001227	53	461	0.002168	103	237.4	0.00421
4	6,113	0.0001636	54	453	0.002209	104	235.1	0.00425
5	4,890	0.0002045	55	445	0.002250	105	232.9	0.00429
6	4,075	0.0002454	56	437	0.002290	106	230.7	0.00434
7	3,493	0.0002863	57	429	0.002331	107	228.5	0.00438
8	3,056	0.000327	58	422	0.002372	108	226.4	0.00442
9	2,717	0.000368	59	414	0.002413	109	224.3	0.00446
10	2,445	0.000409	60	408	0.002554	110	222.3	0.00450
11	2,223	0.000450	61	401	0.002495	111	220.3	0.00454
12	2,038	0.000491	62	394	0.00254	112	218.3	0.00458
13	1,881	0.000532	63	388	0.00258	113	216.4	0.00462
14	1,746	0.000573	64	382	0.00262	114	214.5	0.00466
15	1,630	0.000614	65	376	0.00266	115	212.6	0.00470
16	1,528	0.000654	66	370	0.00270	116	210.8	0.00474
17	1,438	0.000695	67	365	0.00274	117	209.0	0.00479
18	1,358	0.000736	68	360	0.00278	118	207.2	0.00483
19	1,287	0.000777	69	354	0.00282	119	205.5	0.00487
20	1,223	0.000818	70	349	0.00286	120	203.8	0.00491
21	1,164	0.000859	71	344	0.00290	121	202.1	0.00495
22	1,111	0.000900	72	340	0.00294	122	200.4	0.00499
23	1,063	0.000941	73	335	0.00299	123	198.8	0.00503
24	1,019	0.000982	74	330	0.00303	124	197.2	0.00507
25	978	0.001022	75	326	0.00307	125	195.6	0.00511
26	940	0.001063	76	322	0.00311	126	194.0	0.00515
27	906	0.001104	77	318	0.00315	127	192.5	0.00519
28	873	0.001145	78	313	0.00319	128	191.0	0.00524
29	843	0.001186	79	309	0.00323	129	189.5	0.00528
30	815	0.001227	80	306	0.00327	130	188.1	0.00532
31	789	0.001268	81	302	0.00331	131	186.6	0.00536
32	764	0.001309	82	298	0.00335	132	185.2	0.00540
33	741	0.001350	83	295	0.00339	133	183.8	0.00544
34	719	0.001391	84	291	0.00344	134	182.5	0.00548
35	699	0.001432	85	288	0.00348	135	181.1	0.00552
36	679	0.001472	86	284	0.00352	136	179.8	0.00556
37	661	0.001513	87	281	0.00356	137	178.5	0.00560
38	643	0.001554	88	278	0.00360	138	177.2	0.00564
39	627	0.001595	89	275	0.00364	139	175.9	0.00569
40	611	0.001636	90	272	0.00368	140	174.6	0.00573
41	596	0.001677	91	269	0.00372	141	173.4	0.00577
42	582	0.001718	92	266	0.00376	142	172.2	0.00581
43	569	0.001759	93	263	0.00380	143	171.0	0.00585
44	556	0.001800	94	260	0.00384	144	169.8	0.00589
45	543	0.001840	95	257	0.00389	145	168.6	0.00593
46	532	0.001881	96	255	0.00393	146	167.5	0.00597
47	520	0.001922	97	252	0.00397	147	166.3	0.00601
48	509	0.001963	98	249.5	0.00401	148	165.2	0.00605
49	499	0.002004	99	247.0	0.00405	149	164.1	0.00609
50	489	0.002045	100	244.5	0.00409	150	163.0	0.00613

TABLE 1—*Concluded*

Molecular weight	1 mg./l. ppm.	1 ppm. mg./l.	Molecular weight	1 mg./l. ppm.	1 ppm. mg./l.	Molecular weight	1 mg./l. ppm.	1 ppm. mg./l.
151	161.9	0.00618	201	121.6	0.00822	251	97.4	0.01027
152	160.9	0.00622	202	121.0	0.00826	252	97.0	0.01031
153	159.8	0.00626	203	120.4	0.00830	253	96.6	0.01035
154	158.8	0.00630	204	119.9	0.00834	254	96.3	0.01039
155	157.7	0.00634	205	119.3	0.00838	255	95.9	0.01043
156	156.7	0.00638	206	118.7	0.00843	256	95.5	0.01047
157	155.7	0.00642	207	118.1	0.00847	257	95.1	0.01051
158	154.7	0.00646	208	117.5	0.00851	258	94.8	0.01055
159	153.7	0.00650	209	117.0	0.00855	259	94.4	0.01059
160	152.8	0.00654	210	116.4	0.00859	260	94.0	0.01063
161	151.9	0.00658	211	115.9	0.00863	261	93.7	0.01067
162	150.9	0.00663	212	115.3	0.00867	262	93.3	0.01072
163	150.0	0.00667	213	114.8	0.00871	263	93.0	0.01076
164	149.1	0.00671	214	114.3	0.00875	264	92.6	0.01080
165	148.2	0.00675	215	113.7	0.00879	265	92.3	0.01084
166	147.3	0.00679	216	113.2	0.00883	266	91.9	0.01088
167	146.4	0.00683	217	112.7	0.00888	267	91.6	0.01092
168	145.5	0.00687	218	112.2	0.00892	268	91.2	0.01096
169	144.7	0.00691	219	111.6	0.00896	269	90.9	0.01100
170	143.8	0.00695	220	111.1	0.00900	270	90.6	0.01104
171	143.0	0.00699	221	110.6	0.00904	271	90.2	0.01108
172	142.2	0.00703	222	110.1	0.00908	272	89.9	0.01112
173	141.3	0.00708	223	109.6	0.00912	273	89.6	0.01117
174	140.5	0.00712	224	109.2	0.00916	274	89.2	0.01121
175	139.7	0.00716	225	108.7	0.00920	275	88.9	0.01125
176	138.9	0.00720	226	108.2	0.00924	276	88.6	0.01129
177	138.1	0.00724	227	107.7	0.00928	277	88.3	0.01133
178	137.4	0.00728	228	107.2	0.00933	278	87.9	0.01137
179	136.6	0.00732	229	106.8	0.00937	279	87.6	0.01141
180	135.8	0.00736	230	106.3	0.00941	280	87.3	0.01145
181	135.1	0.00740	231	105.8	0.00945	281	87.0	0.01149
182	134.3	0.00744	232	105.4	0.00949	282	86.7	0.01153
183	133.6	0.00748	233	104.9	0.00953	283	86.4	0.01157
184	132.9	0.00753	234	104.5	0.00957	284	86.1	0.01162
185	132.2	0.00757	235	104.0	0.00961	285	85.8	0.01166
186	131.5	0.00761	236	103.6	0.00965	286	85.5	0.01170
187	130.7	0.00765	237	103.2	0.00969	287	85.2	0.01174
188	130.1	0.00769	238	102.7	0.00973	288	84.9	0.01178
189	129.4	0.00773	239	102.3	0.00978	289	84.6	0.01182
190	128.7	0.00777	240	101.9	0.00982	290	84.3	0.01186
191	128.0	0.00781	241	101.5	0.00986	291	84.0	0.01190
192	127.3	0.00785	242	101.0	0.00990	292	83.7	0.01194
193	126.7	0.00789	243	100.6	0.00994	293	83.4	0.01198
194	126.0	0.00793	244	100.2	0.00998	294	83.2	0.01202
195	125.4	0.00798	245	99.8	0.01002	295	82.9	0.01207
196	124.7	0.00802	246	99.4	0.01006	296	82.6	0.01211
197	124.1	0.00806	247	99.0	0.01010	297	82.3	0.01215
198	123.5	0.00810	248	98.6	0.01014	298	82.0	0.01219
199	122.9	0.00814	249	98.2	0.01018	299	81.8	0.01223
200	122.3	0.00818	250	97.8	0.01022	300	81.5	0.01227

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[1] A. C. Fieldner, S. H. Katz, and S. P. Kinney, "Gas Masks for Gases Met in Fighting Fires," *U. S. Bur. Mines, Tech. Paper 248* (1921).

TABLE 2

Limits of Inflammability and Explosive Range[a,b]

Substance	Lower limit, % by vol.	Upper limit, % by vol.	Range
Acetaldehyde, CH_3CHO	*4.0*	*57.0*	53
Acetic acid, CH_3COOH	4.0	—	—
Acetone, CH_3COCH_3	3.0	11	8.0
Acetylene, C_2H_2	2.5	80.0	77.5
Allyl alcohol, $CH_2:CHCH_2OH$	*2.4*	—	—
Ammonia, NH_3	*16.0*	*27.0*	11.0
Amyl acetate, $CH_3COOC_5H_{11}$	1.1	—	—
Amyl alcohol, $C_5H_{11}OH$	*1.2*	—	—
Amyl chloride, $C_5H_{11}Cl$	*1.4*	—	—
Amylene, C_5H_{10}	*1.6*	—	—
Benzene, C_6H_6	1.4	6.8	5.4
Benzine	1.1	—	—
Blast-furnace gas	36	65	29
Butane, C_4H_{10}	1.85	8.4	6.55
Butyl acetate, $CH_3COOC_4H_9$	1.7	—	—
Butyl alcohol, C_4H_9OH	*1.7*	—	—
Butylene, $C_2H_5CH:CH_2$	*1.7*	*9.0*	*7.3*
Butyl methyl ketone, $CH_3COC_4H_9$	*1.2*	*8.0*	6.8
Carbon disulfide, CS_2	1.25	44.0	42.75
Carbon monoxide, CO	12.5	74.0	61.5
Carbon oxysulfide, COS	11.9	28.5	16.6
Coal gas	6	33	27
Cyanogen, $(CN)_2$	6.6	42.6	35.0
Cyclohexane, C_6H_{12}	1.3	8.4	7.1
Cyclopropane, C_3H_6	*2.4*	*10.3*	7.9
Decane, $C_{10}H_{22}$	*0.7*	—	—
Dichloroethylene, $C_2H_2Cl_2$	9.7	12.8	3.1
Dioxane, $C_4H_8O_2$	*2.0*	*22.3*	20.3
Ethane, C_2H_6	3.2	12.5	9.3
Ethyl acetate, $CH_3COOC_2H_5$	*2.2*	*11.4*	9.2
Ethyl alcohol, C_2H_5OH	4.3	19.0[c]	13.7
Ethyl bromide, C_2H_5Br	*6.7*	*11.3*	4.6
Ethyl chloride, C_2H_5Cl	*4.0*	*14.8*	10.8
Ethyl ether, $(C_2H_5)_2O$	1.9	48	46.1
Ethylene, C_2H_4	3.0	29	26.0
1,2-Dichloroethane (ethylene dichloride), $ClCH_2CH_2Cl$	6.2	15.9[d]	9.7
Ethylene oxide, $(CH_2)_2O$	3.0	80.0	77.0
Ethyl formate, $HCOOC_2H_5$	3.5	16.4	12.9
Ethyl methyl ether, $CH_3OC_2H_5$	*2.0*	*10.1*	8.1
Ethyl methyl ketone, $CH_3COC_2H_5$	1.8	10.0	8.2
Ethyl nitrite, C_2H_5ONO	*3.0*	—	—
Ethyl selenide, $(C_2H_5)_2Se$	*2.5*	—	—
Gasoline	1.4	6.0	4.6
Heptane, $CH_3(CH_2)_5CH_3$	*1.0*	*6.0*	5.0
Hexane, $CH_3(CH_2)_4CH_3$	1.2	6.9	5.7
Hydrogen, H_2	4.1	74	70.1
Hydrogen cyanide, HCN	*5.6*	*40.0*	34.4
Hydrogen sulfide, H_2S	*4.3*	*45.5*	41.2
Illuminating gas (manufactured gas)	5–7	21–31	—
Isoamyl alcohol, $C_5H_{11}OH$	*1.2*	—	—

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[a] At atmospheric pressure and ordinary temperature in air.

[b] Values in italics obtained in closed apparatus.

[c] At 60° C.

[d] At 100° C.

TABLE 2—*Concluded*

Substance	Lower limit, % by vol.	Upper limit, % by vol.	Range
Isobutane, $(CH_3)_3CH$	1.8	8.4	6.6
Isobutyl alcohol, $(CH_3)_2CHCH_2OH$	*1.8*	—	—
Isopentane, C_5H_{12}	*1.3*	—	—
Isopropyl acetate, $CH_3COOCH(CH_3)_2$	*1.8*	7.8[d]	6.0
Isopropyl alcohol, C_3H_7OH	*2.6*	—	—
Lead tetramethyl, $Pb(CH_3)_4$	*1.8*	—	—
Methane, CH_4	*5.0*	*15.0*	10.0
Methyl acetate, CH_3COOCH_3	*3.1*	*15.6*	12.5
Methyl alcohol, CH_3OH	6.7	36.5	29.8
Methyl bromide, CH_3Br	13.5	14.5	1.0
Methyl chloride, CH_3Cl	*8.2*	*18.7*	10.5
Methylcyclohexane, $CH_3C_6H_{11}$	1.2	—	—
Methyl formate, $HCOOCH_3$	5.0	22.7	17.7
Methyl propyl ketone, $CH_3COC_3H_7$	1.5	8.2	6.7
Natural gas	4.8	13.5	—
Nonane, C_9H_{20}	*0.83*	—	—
Octane, C_8H_{18}	0.95	—	—
Pentane, $CH_3(CH_2)_3CH_3$	1.4	7.8	6.4
Propane, C_3H_8	2.4	9.5	7.1
Propyl acetate, $CH_3COOC_3H_7$	2.0	*8.0*	—
Propyl alcohol, C_3H_7OH	*2.5*	—	—
Propylene, $CH_2{:}CHCH_3$	*2.0*	*11.1*	9.1
Propylene dichloride, $CH_2ClCHClCH_3$	*3.4*	*14.5*[4]	—
Propylene oxide, C_3H_6O	2.1	21.5	19.4
Pyridine, C_5H_5N	*1.8*	*12.4*	10.6
Sewage tank gases	5.3–8.3	16.0–19.3	—
Tin tetramethyl, $Sn(CH_3)_4$	*1.9*	—	—
Toluene, $C_6H_5CH_3$	*1.3*	*6.8*	5.5
Turpentine	0.8	—	—
Vinyl chloride, $CH_2{:}CHCl$	4.0	21.7	17.7
Vinyl ether, $(CH_2{:}CH)_2O$	*1.7*	*27*	25.3
Water gas	6 to 9	55 to 70	—
o-Xylene, $C_6H_4(CH_3)_2$	*1.0*	*6.0*	5.0

This table was compiled by the author from the following references:

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TABLE 3

Order of Toxicity of Gases and Vapors[1]

Substance	Ppm.	Mg./l.
Phosphine	0.05	0.00007
Arsine	0.05	0.0001
Hydrogen selenide	0.05	0.0001
Stibine	0.1	0.0005
Acrolein	0.5	0.001
Phosphorus trichloride	0.5	0.0028
Nitroglycerin	0.5	0.005
Ozone	1	0.002
Chlorine	1	0.003
Phosgene	1	0.004
Methyl sulfate (dimethyl sulfate)	1	0.005
Sulfur monochloride (sulfur chloride)	1	0.006
Bromine	1	0.006
Nickel carbonyl	1	0.007
Hydrogen fluoride	3	0.0027
Formaldehyde	5	0.006
Hydrogen chloride	5	0.007
Ethylene chlorohydrin	5	0.016
Aniline	5	0.019
Phenol	5	0.019
Acetic anhydride	5	0.021
Toluidine	5	0.022
Cresol	5	0.022
Dimethylaniline	5	0.025
Mononitrotoluene	5	0.028
1,1,2,2-Tetrachloroethane	5	0.034
Hydrogen cyanide	10	0.011
Acetic acid	10	0.025
Sulfur dioxide	10	0.026
1,1-Dichloro-1-nitroethane	10	0.059
Allyl alcohol	15	0.036
Dichloroethyl ether	15	0.083
Hydrogen sulfide	20	0.027
Acrylonitrile	20	0.043
Carbon disulfide	20	0.062
Methyl bromide	20	0.078
1-Chloro-1-nitropropane	20	0.101
Nitrogen oxides (other than nitrous oxide) (as NO_2)	25	0.057
Ethylene glycol monomethyl ether (methyl Cellosolve)	25	0.078
2-Chlorobutadiene (chloroprene)	25	0.091
Ethylene glycol monomethyl ether acetate (methyl Cellosolve acetate)	25	0.121
Isophorone	25	0.141
Benzene (benzol)	35	0.111
Butyl alcohol (*n*-butanol)	50	0.152
Allyl chloride	50	0.156
2-Nitropropane	50	0.182
Mesityl oxide	50	0.201
Diethylene glycol monoethyl ether (Carbitol)	50	0.274
o-Dichlorobenzene	50	0.301
Carbon tetrachloride	50	0.315
1,2-Dichloroethane (ethylene dichloride)	75	0.301
Monochlorobenzene	75	0.345
Ammonia	100	0.076
Carbon monoxide	100	0.120
Ethylene oxide	100	0.180
Methyl chloride	100	0.207
Nitromethane	100	0.250
Methyl formate	100	0.255

TABLE 3—*Concluded*

Substance	Ppm.	Mg./l.
Ethyl formate	100	0.303
Nitroethane	100	0.307
Isoamyl alcohol	100	0.360
Dioxane	100	0.360
Cyclohexanone	100	0.401
1,1-Dichloroethane	100	0.401
Cyclohexanol	100	0.409
Butyl methyl ketone (methyl butyl ketone)	100	0.409
Isobutyl methyl ketone (methyl isobutyl ketone)	100	0.409
Methylcyclohexanol	100	0.466
Chloroform	100	0.487
Methylcyclohexanone	100	0.499
Trichloroethylene	100	0.537
Ethylene glycol monoethyl ether acetate (Cellosolve acetate)	100	0.540
Turpentine	100	*ca.* 0.6
Tetrachloroethylene	100	0.679
Methyl alcohol (methanol)	200	0.262
Acetaldehyde	200	0.360
Methyl acetate	200	0.606
Methyl propyl ketone (2-pentanone)	200	0.704
Ethylene glycol monoethyl ether (Cellosolve)	200	0.736
Toluene (toluol)	200	0.752
1,2-Dichloroethylene	200	0.794
Naphtha (solvent, coal tar)	200	*ca.* 0.8
Propyl acetate	200	0.834
Styrene monomer	200	0.850
Xylene (xylol)	200	0.868
Butyl acetate	200	0.948
Ethylene glycol monobutyl ether (butyl Cellosolve)	200	0.966
Amyl acetate	200	1.064
Ethyl methyl ketone (2-butanone)	250	0.735
Cyclopropane (propene)	400	0.687
Isopropyl alcohol (isopropanol)	400	1.022
Ethyl ether	400	1.212
Cyclohexene	400	1.340
Cyclohexane	400	1.376
Ethyl acetate	400	1.440
Vinyl chloride	500	1.280
Acetone	500	1.186
Dichloromethane	500	1.740
Hexane	500	1.760
Gasoline	500	*ca.* 2.0
Naphtha (petroleum)	500	*ca.* 2.0
Stoddard solvent	500	*ca.* 2.0
Methylcyclohexane	500	2.005
Heptane	500	2.045
Isopropyl ether	500	2.085
Octane	500	2.330
Ethyl alcohol	1,000	1.881
1,3-Butadiene	1,000	2.210
Pentane	1,000	2.940
Dichloromonofluoromethane	1,000	4.21
Dichlorodifluoromethane	1,000	4.95
Trichloromonofluoromethane (Monofluorotrichloromethane)	1,000	5.62
Dichlorotetrafluoroethane	1,000	6.99
Carbon dioxide	5,000	9.0

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[1] Based principally on recommended maximum allowable concentrations for daily 8-hour exposures as given in the report submitted by the Committee on Threshold Limits, American Conference of Governmental Industrial Hygienists (1947 meeting), *Ind. Hyg. Newsletter*, 7, No. 8, 15 (1947); and the meeting in April, 1948.

TABLE 4
Probable Safe Concentration Limits of Exposure for Gases

Substance	1 Gov. hygienists		2 A.S.A., ppm.	3 Calif., ppm.	4 Conn., ppm.	5 Cook, ppm.	6 Mass., ppm.	7 Matt, ppm.	8 N. Y., ppm.	9 Oregon, ppm.	10 U.S.S.R., ppm.	11 Utah, ppm.	12 Wis., ppm.
	ppm.	mg./l.											
Ammonia........	100	0.076	—	100	—	100	100	100–200	100	100	40	100	100
Arsine...........	0.05	0.0001	—	1	—	1	0.05	—	1	0.5	1	1	1
Bromine.........	1	0.006	—	1	—	1	—	0.15–0.3	1	—	—	1	
1,3-Butadiene....	1,000	2.21	—	5,000	—	5,000							
Carbon dioxide...	5,000	9.0	—	5,000	—	5,000	—	—	5,000	5,000	—	5,550	
Carbon monoxide.	100	0.12	100	100	100	100	100	—	100	100	8–16	100	100
Chlorine.........	1	0.003	—	1	1	5	1	1–2	1	1	0.35–0.6	1	1
Cyanogen........	—	—	—	20 (0.043 mg./l.)									
Cyclopropane....	400	0.687	—										
Dichlorodifluoromethane.......	1,000	4.95	—	—	—	100,000							
Dichloromonofluoromethane..	1,000	4.21	—	—	—	5,000							
Dichlorotetrafluoroethane....	1,000	6.99	—	—	—	10,000							
Formaldehyde	5	0.006	10	10	10	10	5	—	5	10	—	20	20
Hydrogen chloride	5	0.007	—	10	10	10	10	10	10	10	—	10	10

Substance	1 Gov. hygienists		2 A.S.A.,	3 Calif.,	4 Conn.,	5 Cook,	6 Mass.,	7 Matt,	8 N.Y.,	9 Oregon,	10 U.S.S.R.,	11 Utah,	12 Wis.,
	ppm.	mg./l.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.	ppm.
Hydrogen cyanide	10	0.011	—	20	20	20	20	—	20	20	—	20	20
Hydrogen fluoride	3	0.0027	—	3	3	3	1.5	—	3	3	—	3	3
Hydrogen selenide	0.05	0.0001	—	0.1	—	0.1							
Hydrogen sulfide.	20	0.027	20	20	20	20	20	—	20	20	2–10	20	20
Nitrogen oxides (other than nitrous oxide) (calcd. as NO_2)	25	0.047	25	25	25	25	10	—	40	—	—	10–40	10
Ozone...........	1	0.002	—	1	—	1	1	—	1	0.5	—	1	1
Phosphine.......	0.05	0.00007	—	1	—	1	1	—	1	1	—	2	2
Stibine..........	0.1	0.0005	—	10	—	1							
Sulfur dioxide....	10	0.026	—	10	10	10	10	—	10	10	3–13	10	10

References:

1. Committee on Threshold Limits, American Conference of Governmental Industrial Hygienists, *Ind. Hyg. Newsletter*, *7*, No. 8, 15 (1947); revision adopted April, 1948.
2. American Standards Association, *Am. Standards* through 1948.
3. State of California, Div. Ind. Safety, Dept. Ind. Relations, "Dusts, Fumes, Mists, Vapors, and Gases," 1948.
4. State of Connecticut, Dept. Health, Sanitary Code, *Regulation 280*, 1948.
5. W. A. Cook, "Maximum Allowable Concentrations of Industrial Atmospheric Contaminants," *Ind. Med.*, *14*, 936 (1945).
6. Massachusetts Dept. Labor Industries, Div. Occupational Hyg., "Maximum Allowable Concentrations," 1948.
7. E. Matt, Dissertation (Wuertzburg, 1889), as quoted by F. Flury and F. Zernik, *Schaedliche Gase*, Springer, Berlin, 1931.
8. New York State, Dept. Labor, Div. Ind. Hyg. These values are not official; they are used by the Div. Ind. Hyg. as a guide.
9. Oregon State Board of Health, "Rules and Regulations for the Prevention and Control of Occupational Diseases," 1945.
10. A. S. Zhitkova, S. I. Kaplun, and J. B. Ficklen, *Poisonous Gases*, Service to Industry, Hartford, 1936.
11. Utah Dept. Health, Ind. Hyg. Div., "Useful Criteria in the Identification of Certain Occupational Health Hazards," 1945.
12. Industrial Commission of Wisconsin, "General Orders on Dusts, Fumes, Vapors, and Gases," 1947.

TABLE 5

Probable Safe Concentration Limits of Exposure for Vapors

Substance	1 Gov. hygienists		2	3	4	5	6	7	8	9	10
	ppm.	mg./l.	A.S.A., ppm.	Calif., ppm.	Conn., ppm.	Cook, ppm.	Mass., ppm.	N. Y., ppm.	Ore-gon, ppm.	Utah, ppm.	Wis., ppm.
Acetaldehyde	200	0.360	—	200	—	200					
Acetic acid	10	0.025	—	10	—	10	—	10			
Acetic anhydride	5	0.021									
Acetone	500	1.186	—	1,000	—	500	500	1,000	500	200	
Acrolein	0.5	0.001	—	0.5	—	0.5	—	—	1	3.3	
Acrylonitrile	20	0.043	—	20	—	20	—	20	20		
Allyl alcohol	—	—	—	15 (0.035 mg./l.)							
Allyl chloride	—	—	—	50 (0.156 mg./l.)							
Amyl acetate	200	1.064	—	200	—	200	200	400	400	400	400
Aniline	5	0.019	—	5	—	5	5	5	5	5–7	
Benzene (benzol)	35	0.111	100	100	100	100	35	50	75	75–100	755
Benzine	—	—	—	1,000 (4.0 mg./l.)	—	500	—	1,000	—	1,000	
n-Butyl acetate	200	0.948	—	200	—	200	200	400	—	—	400
n-Butyl alcohol (butanol)	50	0.152	—	100	—	50	50	200	—	100	
Butyl methyl ketone (methyl butyl ketone)	100	0.409	—	200	—	200					
Carbon disulfide	20	0.062	20	20	20	20	20	20	20	20	15
Carbon tetrachloride	50	0.315	—	100	100	100	50	75	50	100	100
2-Chlorobutadiene (chloroprene)	25	0.091	—	25	—	25	—	—	—	83	
Chloroform	100	0.487	—	100	—	100	—	100	—	100	

Substance	1 Gov. hygienists ppm.	 mg./l.	2 A.S.A., ppm.	3 Calif., ppm.	4 Conn., ppm.	5 Cook, ppm.	6 Mass., ppm.	7 N. Y., ppm.	8 Ore-gon, ppm.	9 Utah, ppm.	10 Wis., ppm.
1-Chloro-1-nitropropane.	20	0.101	—	20	—	20					
Cresols and cresylic acid.	—	—	—	5 (0.022 mg./l.)							
Cyclohexane...........	400	1.376	—	400	—	400					
Cyclohexanol...........	100	0.409	—	100	—	100					
Cyclohexanone..........	100	0.401	—	100	—	100					
Cyclohexene...........	400	1.340	—	400	—	400					
o-Dichlorobenzene.......	50	0.301	—	75	—	75	75	75	75	—	75
1,1-Dichloroethane (ethylidene dichloride)	100	0.401	—	100	—	100					
1,2-Dichloroethane (ethylene dichloride). .	75	0.301	—	100	—	100	75	100	100	100	100
1,2-Dichloroethylene.....	200	0.794	—	100	—	100	—	—	—	100	
Dichloroethyl ether.....	15	0.083	—	15	—	15	15	15	—	15	15
Dichloromethane (methylene chloride)..........	500	1.740	—	500	—	500	—	500			
1,1-Dichloro-1-nitroethane..............	10	0.059	—	—	—	10					
1,2-Dichloropropane (propylene dichloride).	75	0.347									
Diethylene glycol monoethyl ether (Carbitol).	—	—	—	50 (0.274 mg./l.)							
Dimethylaniline.........	5	0.025	—	5	—	5	—	5	5		
Dioxane..............	100	0.360	—	100	—	500					
Ethyl acetate..........	400	1.440	—	400	—	400	400				
Ethyl alcohol..........	1,000	1.881	—	1,000	—	1,000	—	1,000			

Table continued

TABLE 5—*Continued*

	1		2	3	4	5	6	7	8	9	10
	Gov. hygienists										
Substance	ppm.	mg./l.	A.S.A., ppm.	Calif., ppm.	Conn., ppm.	Cook, ppm.	Mass., ppm.	N. Y., ppm.	Ore-gon, ppm.	Utah, ppm.	Wis., ppm.
Ethylbenzene	200	0.868	—	200	—	200					
Ethyl bromide	200	0.900	—	400	—	400	—	—	—	1,700	
Ethyl chloride	1,000	2.640	—	1,000	—	5,000	—	—	—	20,000	
Ethylene chlorohydrin	5	0.016	—	10	—	10					
Ethylene glycol monobutylether (butyl Cellosolve)	200	0.966	—	200	—	200					
Ethylene glycol monoethyl ether (Cellosolve)	200	0.736	—	200	—	200	—	—	—	500	
Ethylene glycol monoethylether acetate (Cellosolve acetate)	100	0.540	—	200	—	100					
Ethylene glycol monomethyl ether (methyl Cellosolve)	25	0.078	—	100	—	100	—	—	—	<25	
Ethylene glycol monomethyl ether acetate (methyl Cellosolve acetate)	25	0.121	—	100	—	100					
Ethylene oxide	100	0.180	—	100	—	100	—	—	—	<250	
Ethyl ether	400	1.212	—	1,000	—	500	400	400	400	400	400
Ethyl formate	100	0.303	—	200	—	200					
Ethyl methacrylate	—	—	—	400 (1.864 mg./l.)							
Ethyl methyl ketone (2-butanone)	250	0.735	—	200	—	200	300				
Ethyl silicate	100	0.851	—	100	—	100					
Gasoline	500	*ca.* 2.0	—	1,000	1,000	500	1,000	100	500	1,000	1,000

Substance	1 Gov. hygienists		2 A.S.A., ppm.	3 Calif., ppm.	4 Conn., ppm.	5 Cook, ppm.	6 Mass., ppm.	7 N. Y., ppm.	8 Ore-gon, ppm.	9 Utah, ppm.	10 Wis., ppm.
	ppm.	mg./l.									
Heptane	500	2.045	—	500	—	500					
Hexane	500	1.760	—	1,000	—	1,000					
Isoamyl alcohol	100	0.360	—	100	—	100	200	—	—	55.6	
Isobutyl methyl ketone (methyl isobutyl ketone)	100	0.409	—	200	—	200					
Isophorone	25	0.141	—	25	—	25					
Isopropyl alcohol	400	1.022	—	400	—	400					
Isopropyl ether	500	2.085	—	500	—	500					
Mesityl oxide	50	0.201	—	50	—	50					
Methyl acetate	200	0.606	—	100	—	100					
Methyl alcohol (methanol)	200	0.262	200	200	200	200	200	200	100	100–200	200
Methyl bromide	20	0.078	—	20	—	20	—	35	35	50	
Methyl chloride	100	0.207	—	200	—	200	—	—	100	500	
Methylcyclohexane	500	2.005	—	1,000	—	1,000					
Methylcyclohexanol	100	0.466	—	100	—	100					
Methylcyclohexanone	100	0.499	—	100	—	100					
Methyl formate	100	0.255	—	400	—	400					
Methyl methacrylate	—	—	—	500 (2.045 mg./l.)							
Methyl propyl ketone (pentanone)	200	0.704	—	400	—	400					
Methyl sulfate	1	0.005	—	1	—	1					
Monochlorobenzene	75	0.345	—	75	—	75	75	75	—	75	75
Mononitrotoluene	5	0.028	—	5	—	5	—	5			

Table continued

TABLE 5—*Continued*

	1 Gov. hygienists		2	3	4	5	6	7	8	9	10
Substance	ppm.	mg./l.	A.S.A., ppm.	Calif., ppm.	Conn., ppm.	Cook, ppm.	Mass., ppm.	N. Y., ppm.	Oregon, ppm.	Utah, ppm.	Wis., ppm.
Naphtha (coal tar, solvent)................	200	*ca.* 0.8	—	100–200	—	100–200	200	—	200		
Naphtha (petroleum)....	500	*ca.* 2.0	—	500	—	500	—	—	500	5,000	
Nickel carbonyl.........	1	0.007									
Nitrobenzene...........	1	0.005	—	5	—	5	5	5	5	1–5	5
Nitroethane............	100	0.307	—	200	—	200					
Nitroglycerin...........	0.5	0.005	—	0.5	—	0.5					
Nitromethane..........	100	0.250	—	200	—	200					
2-Nitropropane.........	50	0.182									
Octane................	500	2.330	—	500	—	500					
Pentane...............	1,000	2.94	—	5,000	—	5,000					
Phenol................	—	—	—	5 (0.019 mg./l.)							
Phosgene..............	1	0.004	—	1	1	1	—	1	1	1	1
Phosphorus trichloride...	0.5	0.0028	—	0.5	—	0.5	—	—	—	0.7	
Propyl acetate..........	200	0.834	—	200	—	200					
Stoddard solvent........	500	*ca.* 2.0	—	500	—	500	—	750			
Styrene monomer.......	200	0.850	400	400	400	400	400	400	400		
Sulfur monochloride.....	1	0.006	—	1	—	1					
1,1,2,2-Tetrachloroethane	5	0.034	—	10	—	10	5	10	10	10	10
Tetrachloroethylene.....	100	0.679	—	200	—	200	200	200	200	200	200
Toluene (toluol)........	200	0.752	200	200	200	200	200	200	200	200	200
Toluidine..............	5	0.022	—	5	—	5					
Trichloroethane.........	—	—	—	50 (0.272 mg./l.)							

TABLE 5—*Concluded*

Substance	1 Gov. hygienists		2 A.S.A., ppm.	3 Calif., ppm.	4 Conn., ppm.	5 Cook, ppm.	6 Mass., ppm.	7 N. Y., ppm.	8 Oregon, ppm.	9 Utah, ppm.	10 Wis., ppm.
	ppm.	mg./l.									
Trichloroethylene	100	0.537	200	200	—	200	200	200	200	200	200
Trichloromonofluoromethane	1,000	5.62	—	—	—	10,000					
Turpentine	100	*ca.* 0.60	—	100	700	200	200	200	200	200	200
Vinyl chloride	500	1.280	—	1,000	—	1,000	—	—	—	500	
Xylene (xylol)	200	0.868	200	200	200	200	200	200	200	200	200

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1. Committee on Threshold Limits, American Conference of Governmental Industrial Hygienists, *Ind. Hyg. Newsletter*, *7*, No. 8, 15 (1947); revision adopted April, 1948.
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5. W. A. Cook, "Maximum Allowable Concentrations of Industrial Atmospheric Contaminants," *Ind. Med.*, *14*, 936 (1945).
6. Massachusetts Dept. Labor Industries, Div. Occupational Hyg., "Maximum Allowable Concentrations," 1948.
7. New York State, Dept. Labor, Div. Ind. Hyg. These values are not official; they are used by the Div. Ind. Hyg. as a guide.
8. Oregon State Board of Health, "Rules and Regulations for the Prevention and Control of Occupational Diseases," 1945.
9. Utah Dept. Health, Ind. Hyg. Div., "Useful Criteria in the Identification of Certain Occupational Health Hazards," 1945.
10. Industrial Commission of Wisconsin, "General Orders on Dusts, Fumes, Vapors, and Gases," 1947.

TABLE 6

Probable Safe Concentration Limits of Exposure for Toxic Dusts, Fumes, and Mists
(Mg. per Cubic Meter)

Substance	1 Gov. hygienists	2 A.S.A.	3 Calif.	4 Conn.	5 Cook	6 Mass.	7 N. Y.	8 Oregon	9 Utah	10 Wis.
Antimony	0.5									
Arsenic (except volatile hydrides)	0.5	0.15	3.0	—	0.15	0.15	0.15	0.15	0.5	
Barium	0.5									
Barium peroxide as Ba	—	—	0.5	—	0.5	—	0.5			
Cadmium	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Chlorides	—	—	15.0							
Chlorinated diphenyl oxide	—	—	1.0							
Chlorodiphenyl	1	—	1	—	1	1–5	1	—	—	1.0
Chloronaphthalenes	—	—	—	—	—	1–5	—	—	—	1–5
Chromic acid and chromates as CrO_3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cyanide as CN	5									
Dinitrotoluene	1.5	—	1.5	—	1.5	—	1.5			
Fluorides	2.5	—	2.0	—	—	1	—	2		
Hexachloronaphthalene	—	—	0.5							
Hydrochloric acid mist	—	—	2.0							
Iodine	1.0	—	1	—	1	—	1	0.5–1.0		
Iron oxide fume	15	—	10.0	—	30	—	30			
Lead	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Magnesium oxide fume	15	—	—	—	15	—	—	—	15	
Manganese	6	6	6	6	6	6	6	6	5–50	
Mercury	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Metal fumes (total)	—	—	30							
Nitric acid	—	—	2.0							

TABLE 6—*Concluded*

Substance	1 Gov. hygienists	2 A.S.A.	3 Calif.	4 Conn.	5 Cook	6 Mass.	7 N. Y.	8 Oregon	9 Utah	10 Wis.
Pentachloronaphthalene	0.5	—	1.0	—	0.5	—	0.5	0.5	0.5	
Pentachlorophenol	0.5									
Phosphorus (yellow or white)	0.1									
Phosphorus pentachloride	1									
Phosphorus pentasulfide	1									
Selenium compounds as selenium (except volatile selenides)	0.1									
Sulfuric acid	1.0	—	5	—	5	—	5	—	2	
Tellurium	0.1	—	—	—	0.01					
Tetrachloronaphthalene	—	—	1.0							
Tetryl	1.5	—	1.5	—	1.5					
Trichloronaphthalene	5	—	5.0	—	5	—	5	5	5	
Trinitrotoluene	1.5	—	1.5	—	1.5					
Zinc oxide	15	—	15	—	15	15	15	—	15	15

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TABLE 7

Probable Safe Limits of Exposure for Certain Industrial Dusts

Dust or locality	Safe limit, MPPCF[a]	Free silica, %	Size	Reference
Alundum	50			8
Anthracite coal	50	3		1
Anthracite mines (haulage way)	10–15	13		1
Anthracite mines (rock workers)	5–10	35		1
Asbestos (textile)	5			2
Asbestos	5		0.5–10 μ	3, 8, 9
Asbestos	10		0.5–10 μ	4
Australia	14	10–17		5
Carborundum	50			8
Cement	15			3
Dusts (other than silica or those of toxic nature)	50	<5	0.5–5 μ	4, 8
Dust, total	50	<5	0.5–10 μ	3, 8
Dust, foundry	25			9
Gold mines (Ontario)	8.5	about 35 in rock		5
Granite	15			9
Granite (Barre)	10–20	35		6
Mica	50	<5		8
Organic	50		0.5–5 μ	3
Portland cement	50			8
Pottery	4			3
Sandstone (Australia)	6	90		5
Silica	50	<5		8
Silica	10	25–35	0.5–5 μ	3
Silica	5	over 75	0.5–10 μ	3, 8
Silverware	12			7
Slate	15			3
Slate	50	<5		8
Soapstone	50	<5		8
South Africa	4.5	80		5
Talc	15			3
Talc	20			8

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[a] Million particles per cubic foot.

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